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CONTENTS.

	Page
On some of the Products of the Action of Nitric Acid on Castor Oil. By Thomas George Tilley, Esq.	1
On Bleaching Salts. By M. Detmer, Esq.	6
On the Atomic Weight of Carbon. By Professors Redtenbacher of Prague, and Liebig of Giessen	9
On Malic Acid, and the Changes undergone by its Salts at High Temperatures. By Robert Hagen, Ph.D.	28
Table of the successive Strengths of Pyroxylic Spirit, corresponding to its successive Specific Gravities, with some Introductory Observations. By Andrew Ure, M.D., &c.	36
On the Ferrocyanides. By R. Corbett Campbell, Esq. Communicated by Dr. Clark	38
Examination of Cetine, Ethal, Oils of Laurel Turpentine, Hyssop, and Assafœtida. By John Stenhouse, Ph.D.	43
On the Radical of the Cacodyl Series of Compounds. By Professor Bunsen of Marburg	49
On the employment of Chromic Acid as an Agent in Voltaic Arrangements. By Robert Warington, Esq.	61
On a new Class of Cacodyl Compounds containing Platinum. By Professor Bunsen of Marburg	63
On some of the Substances contained in the Lichens employed for the preparations of Archil and Cudbear. By Edward Schunck, Esq., Manchester	71
On a Re-arrangement of the Molecules of a Body after Solidification. By Robert Warington, Esq.	77
On the Conversion of Benzoic Acid into Hippuric Acid in the Animal Economy. By Alfred Baring Garrod, Esq., of University College	79
On the Constitution of the Sulphates as illustrated by late Thermometrical Researches. By Thomas Graham, Esq., F.R.S. &c.	82
On the Change of Colour in the Biniodide of Mercury. By Robert Warington, Esq.	85
On a new Oxalate of Chromium and Potash. By Henry Croft, Esq.	89
Some additional Observations on the Red Oxalate of Chromium and Potash. By Robert Warington, Esq.	93
On the Preparation of Cyanide of Potassium, and on its Applications. By Prof. Liebig of Giessen.	94
On the Preparation of Artificial Yeast. By George Fownes, Ph.D.	100
On some Salts of Cadmium. By Henry Croft, Esq.	104
Experiments on the Heat disengaged in Combinations. By Thomas Graham, Esq., F.R.S. &c.	106

Page

On Pyrogallic Acid, and some Astringent Substances which yield it. By John Stenhouse, Ph.D. 127

On some Astringent Substances as Sources of Pyrogallic Acid. By John Stenhouse, Ph.D. (*continued*). 132

On some new cases of Voltaic Action, and on the Construction of a Battery without the use of Oxidizable Metals. By Alexander R. Arrott, Esq. 142

On Æthogen and Æthonides. By William H. Balmain, Esq. 149

Report of some Experiments with Saline Manures containing Nitrogen, conducted on the Manor Farm, Havering-atte-Bower, Essex, in the occupation of Collinson Hall, Esq. By W. M. F. Chatterley, Esq. 152

On the Sugar of the Eucalyptus. By James F. W. Johnston, Esq., M.A., F.R.S. 159

On Palladium—its Extraction, Alloys, &c. By William John Cock, Esq. 161

On the Formation of Fat in the Animal Body. By Justus Liebig, Ph.D., M.D., F.R.S. &c. 164

On the Changes in Composition of the Milk of a Cow, according to its Exercise and Food. By Lyon Playfair, Ph.D. 174

On a new Method of obtaining pure Silver, either in the Metallic State or in the form of Oxide. By William Gregory, M.D., F.R.S.E. &c. 190

The Leaf-stalks of Garden Rhubarb as a Source of Malic Acid. By Thomas Everitt, Esq. 193

Observations on M. Reiset's Remarks on the New Method for the Estimation of Nitrogen in Organic Compounds, and also on the supposed part which the Nitrogen of the Atmosphere plays in the formation of Ammonia. By H. Will, Ph.D. 197

Examination of Astringent Substances. By John Stenhouse, Ph.D. (*continued*) 208

On Theine and its Preparation. By John Stenhouse, Ph.D. 215

On the Constitution of the Subsalts of Copper.—No. I. On the Subsulphates. By J. Denham Smith, Esq. 221

On the Spontaneous Change of Fats. By W. Beetz, Esq. 230

On certain Improvements in the Instrument, invented by the late Dr. Wollaston, for ascertaining the Refracting Indices of Bodies. By John Thomas Cooper, Esq. 234

On Theine. By John Stenhouse, Ph.D. 237

On the Composition of an Acid Oxide of Iron (*Ferric Acid*). By J. Denham Smith, Esq. 240

On the Action of Alkalies on Wax. By Robert Warington and William Francis, Esqrs. 248

On the Action of Oil of Vitriol upon Ferrocyanide of Potassium. By George Fownes, Ph.D. 251

MEMOIRS

OF

THE CHEMICAL SOCIETY.

I. *On some of the Products of the Action of Nitric Acid on Castor Oil.* *By* THOMAS GEORGE TILLEY.

Read April 27, 1841.

THE action of nitric acid on the fat acids is a subject that has been lately investigated by Laurent* and Bromeis†, and the interesting results obtained by them having called the attention of chemists to the subject, I was induced, at the suggestion of Professor Liebig, to examine in his laboratory the products of the oxidation of the oil of *Ricinus Communis*, differing as it does in such a remarkable degree from the other fixed oils.

One part of this oil was accordingly mixed with twice its weight of nitric acid diluted with an equal bulk of water, and subjected to a gentle heat in a retort. The parts which distilled over were preserved. After some time the action became very violent, and gas was formed in such quantities as to expel the contents of the retort forcibly from its mouth. The retort must then be removed from the fire, when the action gradually subsides. When again placed on the fire, protected by a sand-bath, the action is not so violent. The process of oxidation must be continued for some days, more or less, according to the strength of the nitric acid employed. When the quantity of nitrous acid fumes decreases, the retort is removed from the fire. In the receiver are found nitric acid, water, and a peculiar volatile oily acid, which new compound will form the subject of the following pages. If the

* *Ann. de Chim. et de Phys.*, lxvi.

† *Annalen der Pharmacie*, xxxv. p. 86. [Noticed in Philosophical Magazine for February, vol. 18. p. 115.]

fatty mass which remains in the retort be mixed with water and distilled, an additional quantity of the acid will be obtained.

It must be separated from the acid fluid on which it floats, mixed with water and redistilled, which process must be repeated several times. After this it must be dried by standing over melted phosphoric acid, chloride of calcium not being adapted to the purpose, it being a little soluble in the acid.

The acid procured in this way is perfectly colourless and transparent, having an agreeable aromatic smell and a sweet stimulating taste. It is sparingly soluble in water, imparting to that fluid its peculiar smell. It is soluble in nitric acid, alcohol and æther. When raised to the temperature of 148° C. it begins to boil, and a small part distils over; but if kept for some time at that temperature, it becomes black and is decomposed, giving off empyreumatic products, so that it cannot be distilled alone. It burns with a clear flame, giving little smoke. It does not become solid though cooled to −17° C. To this body I have given the name of *Œnanthylic Acid*, for reasons which will be stated in another part.

To determine its composition the acid was burned with oxide of copper.

1st. 0·3305 substance gave 0·7810 carbonic acid, and 0·3330 water.

2nd. 0·4295 substance gave 0·9905 carbonic acid, and 0·4009 water.

This gives in 100 parts,

	1st.	2nd.
Carbon.....	65·34	65·33
Hydrogen.....	10·83	10·60
Oxygen.....	23·83	24·07
	100·00	100·00

Œnanthylic Æther.—This æther is formed by dissolving the acid in strong alcohol, and passing a stream of hydrochloric acid gas through the solution. To the mixture is then added carbonate of potash, in order to neutralize all free acid; it is then distilled. The æther passes over into the receiver, and may be freed from any alcohol that it may contain by agitation with water. It must, lastly, be distilled over chloride of calcium in a stream of carbonic acid gas, as it is decomposed by the oxygen of atmospheric air, at the temperature of its boiling point.

The œnanthylic æther so obtained is a colourless fluid, lighter than water, having a peculiar and agreeable smell not unlike that of nitrobenzide. It has a sweet and somewhat

pungent taste, leaving a disagreeable sensation on the palate. It is soluble in æther and alcohol, and burns with a clear blue flame, giving out no smoke. It is solid at the temperature produced by a mixture of snow and salt, and is then crystalline.

Burnt with oxide of copper, 0·2195 substance gave 0·5485 carbonic acid, and 0·3195 water; making in 100 parts,

Carbon.....	68·57
Hydrogen	11·57
Oxygen	19·86
	100·00

and leading to the following composition:—

			Per cent.
18 atoms	Carbon ..... =	1375·80	68·71
18 „	Hydrogen .. =	224·63	11·22
4 „	Oxygen ..... =	400·00	20·07
		2000·43	100·00

Now supposing this æther to be composed of one atom oxide of æthyl and one atom of anhydrous acid, we have for the composition of the latter $C^{14}\,H^{13}\,O^{3}$, and adding to this one atom of water to form the hydrate, we have, in 100 parts,

			Per cent.
14 atoms	Carbon ..... =	1070·09	65·06
14 „	Hydrogen ... =	174·71	10·62
4 „	Oxygen ..... =	400·00	24·32
		1644·80	100·00

which calculated result agrees with the numbers found by actual experiment given at page 2.

Œnanthylate of Silver.—This salt may be easily prepared by precipitating a neutral ammoniacal solution of the acid by nitrate of silver; it falls in the form of a white flocculent powder.

1st. 0·7165 of this salt gave ·3265 silver, which is equivalent to 0·3509 oxide of silver. This gives per cent.,

Oxide of silver.....	48·89
Œnanthylic acid.....	51·11
	100·00

making the atomic weight of the anhydrous acid 1517·0, the calculated result being 1532·33.

By burning the salt dried *in vacuo* over sulphuric acid, with oxide of copper, 0·7350 gave 0·9360 carbonic acid, and 0·3675 water.

2nd. 0·8785 gave 1·1300 carbonic acid, and 0·4505 water. This gives in 100 parts,

	1st.	2nd.
Carbon.....	35·20	35·56
Hydrogen	5·55	5·68
Oxygen.....	10·27	9·78
Oxide of silver.	48·89	48·98
	100	100

and leads to the following theoretical composition:—

				Per cent.
14	atoms	Carbon	1070·090	35·86
13	„	Hydrogen.....	162·233	5·43
3	„	Oxygen.....	300·000	10·07
1	„	Oxide of silver.	1451·061	48·64
		Atomic weight...	2983·384	100·00

The formula for this salt is then $C^{14}\ H^{13}\ O^{3} + Ag\ O$.

Œnanthylate of Baryta.—This salt is formed by boiling carbonate of baryta with an alcoholic solution of œnanthylic acid till the fluid no longer possesses acid reaction. The solution must be filtered while hot, and on cooling deposits the salt in beautiful pearly scales, which are insoluble in æther, but soluble in water and alcohol.

0·3520 of this salt gave 0·1735 carbonate of baryta, or 0·1346 baryta, the atomic weight of the acid, calculated from this, being 1545·54. It gives in 100 parts,

38·23 oxide of barium
61·77 œnanthylic acid
100·00

1st. 0·4395 of the same salt, burned with oxide of copper, gave 0·6645 carbonic acid, and 0·2740 water.

2nd. 0·3460 salt gave 0·5200 carbonic acid, and 2190 water.

After adding to the carbon that which remained, combined as carbonic acid, with the baryta in the combustion tube, we obtain in 100 parts,

Carbon.....	44·84	44·58
Hydrogen.....	6·91	6·87
Oxygen.....	10·02	10·32
Baryta	38·23	38·23
	100·00	100·00

which gives the following theoretical numbers:—

			Per cent.
14 atoms	Carbon	= 1070·09	42·98
13 „	Hydrogen.	= 162·23	6·51
3 „	Oxygen.	= 300·00	12·07
1 „	Oxide of barium	= 956·88	38·44
		2489·20	100·00

It will be seen by the preceding numbers that an excess of carbon is found; but this may be accounted for by the high temperature required to burn the last particles of carbon, by which some of the carbonic acid might have been driven off from the carbonate of baryta in the combustion tube.

The formula for this salt is one atom œnanthylic acid and one atom oxide of barium, or $C^{14} H^{13} O^3 + Ba O$.

Œnanthylate of Potash is obtained by neutralizing the carbonate of that alkali by œnanthylic acid; it does not crystallize, but, on evaporation, assumes the form of a thick transparent jelly.

The *Copper Salt* crystallizes in beautiful needles of a rich green colour, soluble in alcohol, and sparingly so in water.

The *Œnanthylate of Strontian* appears in the form of bright pearly scales, very much resembling the analogous salt of baryta.

It will at once be perceived by the analyses which have been given, that the composition of anhydrous œnanthylic acid is $C^{14} H^{13} O^3$, and it enters as such into the following combinations:—

Œnanthylate of water.....	$C^{14} H^{13} O^3 + H^2 O$
„ oxide of æthyl.	$C^{14} H^{13} O^3 + C^4 H^5 O$
„ „ barium	$C^{14} H^{13} O^3 + Ba O$
„ „ silver .	$C^{14} H^{13} O^3 + Ag O$.

Now it was discovered some time ago that wine owes its peculiar smell to a certain acid in combination with oxide of æthyl. To this acid Liebig and Pelouze, its discoverers, gave the name œnanthic acid (flower of wine). Œnanthic acid has the following composition, $C^{14} H^{13} O^2 + aq$.

The analogy between this acid and the one described in this paper will at once be seen, and the composition of the two acids would lead us to suppose that they are oxides of the same radical, which may for the present be considered as composed of $C^{14} H^{13}$; while the two acids are respectively

$$R + 2\,O$$
$$R + 3\,O.$$

On these grounds I have given the higher oxide the name *Œnanthylic acid*, and propose for the lower oxide, that of

Liebig and Pelouze*, the name *Œnanthylous acid.* It is not improbable that œnanthylic acid may be identical with the azoleinic acid of Laurent†; but he did not obtain it in a state of purity. When the œnanthylate of silver is distilled, there pass into the receiver an oil and a solid body, neither of which possesses acid properties. The solid body is soluble in hot alcohol, and on being allowed to cool, it crystallizes in beautiful needles.

Suberic acid is another product of the oxidation of castor oil; it remains in the retort mixed with oxalic acid: it may be purified by repeated crystallizations, and boiling with nitric acid.

Thus obtained and dried at 100° C., 0·2710 substance gave ·5490 carbonic acid, and 0·1990 water, or, in 100 parts,

	Found.	Atoms.	Calculated.
Carbon . . .	55·97	8	55·64
Hydrogen .	8·15	7	8·03
Oxygen . . .	35·78	4	36·33
	100·00		100·00

giving the formula $C^8 H^6 O^3$ + aq.

The other acids found by Laurent did not appear to have been formed; but this is not affirmed with positive certainty, as the examination was not proceeded with. A trace of lipinic acid, however, may be obtained during the evaporation of the fluid parts, pressed from the suberic acid.

II. *On Bleaching Salts. By* M. Detmer, *Esq.*

Read April 27, 1841.

A SHORT time ago a notice was published by M. Millon on the Bleaching Salts of Chlorine, in which a new view was offered of the constitution of these compounds. They have for some time past generally been considered as compounds or mixtures of a metallic chloride with a hypochlorite of a metallic oxide; bleaching powder or the chloride of lime, for instance, as consisting of chloride of calcium and hypochlorite of lime, in single equivalents, the acid of the last salt containing one atom of oxygen to one atom of chlorine. The reaction of chlorine upon lime supposed, may be very simply stated: two atoms of lime take up two of chlorine; one atom

* *Ann. de Chim. et de Phys.*, t. lxiii. 118. † *Ibid.*, t. lxvi. 172.

only of the lime is decomposed, of which the calcium and oxygen respectively unite with an atom each of chlorine, forming chloride of calcium and hypochlorous acid. The hypochlorous acid combines with the other atom of lime.

Starting from the composition of chlorochromic and chlorosulphuric acids, which are represented by Walter and Regnault as chromic and sulphuric acids in which the third proportion of oxygen is replaced by chlorine ($Cr O_2 + Cl$ and $S O_2 + Cl$), Millon supposes that the bleaching chlorides have a similar relation to the peroxides of their metals. The peroxide of calcium being $Ca O_2$, or $Ca O + O$, bleaching powder is $Ca O + Cl$, or the peroxide of calcium, with chlorine substituted for its second proportion of oxygen. In support of this view Millon adduces observations of his own on the composition of the bleaching compounds of chlorine with different metallic oxides, such as oxides of lead and protoxide of iron, as well as potash, soda and lime, in which the proportion of chlorine was found to vary, but to correspond with the excess of oxygen above one equivalent in the peroxides of the same metals. In particular, potash was found to absorb two equivalents of chlorine, and soda only one, the peroxide of potassium being $K O + 2 O$, while the peroxide of sodium is $Na O + O$.

The attention of the author was particularly directed to ascertain the accuracy of the latter statement. A solution of carbonate of soda was charged with chlorine gas till it acquired a yellow colour and retained not a trace of carbonic acid. The solution was then briskly agitated with air, by which the excess of free chlorine escaped. In analyzing the solution afterwards, one portion of it was treated with a few drops of ammonia, and the chlorine afterwards precipitated by nitrate of silver; another portion was evaporated to dryness for the sodium, which was obtained in the state of chloride of sodium.

In four experiments the liquids charged with chlorine contained chlorine and sodium in the following proportions, in 100 parts: —

Sodium.....	47·88	45·26	46·81	44·76
Chlorine....	52·12	54·74	53·19	55·24,

while, if the bleaching chloride of soda contained 1 eq. of chlorine to 1 eq. of soda, its composition would be

1 eq. sodium.....	46·91
1 eq. chlorine.....	53·09
	100·00

The results correspond as closely as could be expected with this theoretical statement. There can be no doubt then that the chloride of soda contains one of chlorine to one of

soda. This is the result required by Millon's theory, the peroxide of sodium containing, according to him, one of oxygen and one of soda; but it is equally consistent with Balard's theory that the salt is a mixture of single equivalents of chloride of sodium and hypochlorite of soda. To determine the quantity of chlorine which water dissolves, a stream of the gas was sent through water at 59° for five hours. One hundred grammes of water were found to take up 0·663 gramme of chlorine; or 200 cubic inches of water dissolved 207 cubic inches of gas. The chlorine was estimated by converting it into hydrochloric acid by the addition of a few drops of ammonia, slightly acidulating afterwards by nitric acid, and precipitating by nitrate of silver. A solution of 2·58 chloride of potassium in 38·96 water was found to dissolve less chlorine than pure water, in the proportion of 180 to 257. Chlorine gas being allowed to stream through a solution of 9·245 grammes carbonate of potash in 96·495 grammes of water, till saturation, the solution lost all its carbonic acid and took up 6·631 grammes of chlorine. Here 1 eq. of potash = 590 has taken up 656 chlorine, which is very nearly $1\frac{1}{2}$ eq. of chlorine = 663. But when the quantity of free chlorine in the liquid is deducted, the latter is found to contain only 1·34 equivalents of chlorine to 1 eq. of potash. In two other experiments, in which the liquid was agitated with air after being saturated with chlorine, to allow the excess of gas to escape, there were found to 1 eq. of potash 1·44 and 1·43 equivalents of chlorine. The carbonate of potash, therefore, without doubt, takes up more than a single equivalent of chlorine. But the quantity of chlorine combined with the potash is still greatly short of two equivalents, the proportion required by M. Millon's theory; the peroxide of potassium containing two oxygen to one potash, or $K O_2$. The conclusion therefore is inadmissible, that the chloride of potash is analogous in constitution to the peroxide of potassium.

It remains to account for the property which potash is found to possess of taking up more chlorine than is necessary to convert it into chloride of potassium and hypochlorite of potash. On transmitting chlorine through carbonate of potash, a stage in the absorption is very observable, at which the liquid becomes all at once of a yellow colour. This happens when what remains of the potash is entirely converted into bicarbonate of potash. The suddenness of the appearance of the yellow colour appears to be due to a reaction of the carbonic acid upon the hypochlorite of potash in solution, by which hypochlorous acid is set free and tinges the liquid. By the continued application of chlorine to the bicarbonate of

potash, it is converted into a mixture of chloride of potassium, hypochlorite of potash, and free hypochlorous acid. By the ultimate action of the chlorine all the bicarbonate of potash is decomposed, the carbonic acid entirely expelled, and a portion of hypochlorous acid remains free in solution.

This formation of free hypochlorous acid does not occur with carbonate of soda, owing to the much weaker affinity which that base has for carbonic acid, and its forming a much less stable bicarbonate than potash does. The free carbonic acid cannot therefore react upon the hypochlorite of soda, and liberate hypochlorous acid as the free carbonic acid does upon the hypochlorite of potash. The same formation of free hypochlorous acid occurs in a more striking degree when chlorine is sent through a solution of acetate of potash; that solution, it is well known, absorbs a large quantity of gas, and acquires the strong yellow colour, the odour, and all the other properties of free hypochlorous acid. It is here evident, that by the action of chlorine upon acetate of potash, chloride of potassium is formed, with the binacetate of potash, free hypochlorous acid, and the hypochlorite of potash. If the large absorption of chlorine by carbonate of potash is due to carbonic acid, it follows that caustic potash should not absorb any excess of chlorine, but that the property should be confined to the carbonate. Accordingly, in two experiments, the proportion of chlorine absorbed by caustic potash was found to be as nearly as possible a single equivalent. In one experiment 449·1 chlorine, in the other 424·8 chlorine were taken up, instead of 442·6 chlorine, by a single equivalent or 589·9 of potash. Caustic potash, therefore, dissolves no more chlorine than caustic soda. There appears therefore to be no reason to abandon the old theory, that the bleaching solutions of chlorine in alkalies and alkaline earths contain a chloride and hypochlorite, for these bleaching compounds certainly do not correspond with metallic peroxides, as has been lately maintained.

III. *On the Atomic Weight of Carbon. By Professors* Redtenbacher *of Prague, and* Liebig *of Giessen**.

Read May 8, 1841.

In the analysis by combustion of organic substances which contain carbon and hydrogen, the observation has frequently been made of late years, that the weight of the ele-

* Translated from the original German by Dr. J. H. Gilbert.

ments separately found by experiment, actually exceeds the original weight of the matter submitted to combustion. In the analyses we possess of naphthalin by Mitscherlich, by Dumas, and by Woskresensky, this is particularly remarkable. One hundred parts of naphthalin gave to Mitscherlich,—

	1.	2.
Carbon	94·34	94·440
Hydrogen	6·26	6·225
	100·60	100·665

One hundred parts of naphthalin gave to Dumas,—

	1.	2.	3.	4.	5.
Carbon ...	94·2	94·22	94·27	91·9	94·9
Hydrogen	6·3	6·30	6·26	6·2	6·1
	100·5	100·52	100·53	101·1	101·0

And to Woskresensky, 100 parts of the same substance yielded—

	1.	2.	3.	4.	5.	6.
Carbon	94·625	94·598	95·0268	93·668	94·395	94·494
Hydrogen	6·528	6·289	5·3830	6·142	6·206	6·526
	101·153	100·897	100·4098	99·810	101·601	101·020

This constant occurrence in so many carefully conducted experiments, indicates a common source of error upon which it is dependent; it can only be attributed to two causes. One of these may be sought in the defects of the method of analysis, the other in the supposition that the products of the combustion (water and carbonic acid) have different compositions from those usually assigned to them. If indeed either water or carbonic acid contains somewhat less of hydrogen or of carbon than we at present suppose, then as we calculate from the quantities found of the former bodies, the excess in the analyses is diminished in the same proportion.

Let us suppose, for example, that carbonic acid contains only 76 carbon instead of 76·437 to 200 of oxygen, and water only 12 hydrogen instead of 12·4795 to 100 oxygen, and then we shall have no excess in any of the analyses quoted, whilst the experimental come to agree perfectly with the calculated results. Are we then entitled to make such changes in the atomic weights, proceeding as we do upon the assumed accuracy of experiments, which, from the complex nature of the apparatus, can make no claim to absolute precision; or

ought we not first to compare these with other experiments, in which this source of error is entirely avoided?

A question also arises whether *naphthalin*, a substance the atomic weight of which cannot be determined with certainty, as it enters undecomposed into no combination, is a proper substance to select as the means of determining the atomic weight of carbon or of hydrogen? That body must indeed be rejected on this account, for it is not in our power to control our analytical results from a knowledge of the weight of its atom, that is, the sum of the atomic weights of the elements composing it.

When we also consider that the naphthalin, which in the above experiments was submitted to combustion in a glass tube with oxide of copper, is a volatile body, that it cannot be introduced into the combustion tube, with oxide of copper that is absolutely free from moisture; and bear in mind also, that, owing to the volatility of the substance, this moisture cannot previously to combustion be removed by means of exhaustion, we cannot doubt the existence of a source of error, which must increase the per centage of hydrogen beyond that which actually existed in the substance; for, however small the quantity of this hygroscopic moisture may be, it is nevertheless always present; it is weighed with the chloride of calcium tube, and its hydrogen added to that contained in the substance.

In all analyses hitherto conducted, even those in which the whole of the hygroscopic water had been removed as nearly as possible before combustion, by means of exhaustion, it is observed that the experiment invariably gives rather more hydrogen than is indicated by calculation. This excess amounts in good analyses to from 0·1 to 0·2 per cent. It is found, however, that this, in reference to the quantity of substance employed in analysis, is not sufficient to affect the proportion of the elements, to the extent observed in the analyses of naphthalin; the excess in those analyses is however diminished, when allowance is made in the calculation for this error.

There exists therefore some other cause affecting the determination of the equal quantity of the elementary constituents of an organic substance, in such a manner, that one of them, namely, the *carbon*, when calculated from the quantity of carbonic acid obtained by combustion, amounts to more than the weight of the carbon which is contained in the matter analysed. On this account a new determination of the *atomic weight of carbon* appears to be indispensable, and we have united, in

order conjointly to submit the atomic weight of carbon as at present received, to a severe and accurate scrutiny.

It is known that two of the most distinguished natural philosophers, Biot and Arago, have by means of the direct weighing of carbonic acid, fixed upon the number 1·519 for the specific gravity of that gas. Their experiments were repeated by Dulong and Berzelius, with whom, as regards skill and talent, conscientiousness and accuracy, no others can be compared. The two last observers found the number 1·524 for the specific gravity of carbonic acid; that obtained by De Saussure is 1·5269.

The atomic weight of carbon, as calculated from the first of these, is 75·530, and from the other, 76·437. There is no known gas more easily obtained in a pure state, or which can more easily be distinguished from a foreign body, than carbonic acid. Any admixture of atmospheric air, or of other gases, can only lower its specific gravity.

Experiments have lately been conducted by Rudberg on the dilatation of gases under the influence of heat*, from which he calculates that the coefficient of dilatation is somewhat less than was previously supposed; should these experiments be correct, the proof of which still remains to be made known, they do not influence the specific gravities of two gases as determined at the same temperature, even supposing the reduction to the normal temperature be made according to the coefficient of dilatation as hitherto received; if weighed at unequal temperatures, however, a difference is observed.

In the experiments of Dulong and Berzelius, atmospheric air was weighed at $20\frac{1}{2}^{\circ}$ C., and carbonic acid at 18° C., consequently the reduction of the gas to 0° C., according to the former coefficient of dilatation, gives the weight of air somewhat too high, and since this, in an equal volume, represents the *divisor*, the specific gravity of carbonic acid is estimated rather too low; in all cases, however, the differences fall within the limits of the errors of observation.

When we remember that the determinations of the specific gravities of these gases were conducted with the same balloon, the same scales and weights, and at temperatures varying very little from each other, we ought not to call in question their correctness without the strongest and most convincing reasons.

During the last twelve years, a great number of weighings of the vapours of volatile bodies very rich in carbon, have been undertaken in reference to this point by Gay-Lussac,

* See Taylor's Scientific Memoirs, vol. 2, pp. 507, 514, 543.

and also by Dumas; as, for instance, those of alcohol, æther, and acetone, the results of which agree either perfectly with the specific gravity of carbon vapour, as deduced from that of carbonic acid and of oxygen, or indicate it to be somewhat higher; thus the specific gravity of æther vapour is 2·586 by experiment, and 2·580 by calculation; and that of the vapour of alcohol is 1·6133 by experiment, and 1·600 by calculation.

In most of the observations of Dumas, the observed specific gravity of bodies very rich in carbon, is far higher than that obtained by calculation. Thus, according to the formula $C_5\ H_2$, the specific gravity of the vapour of naphthalin is 4·4882; the experiment of Dumas, however, gives 4·528, and that of Woskresensky 4·672, from which it may with great probability be concluded, that the specific gravity of carbon vapour is rather higher than 0·42139, or 0·84279.

The above-mentioned atomic weights of carbon, which have resulted from direct experiments, are contradicted by one, which, however, we may say is quite fictitious; its adoption is based on the hypothesis that the atomic weights of simple bodies are multiples of that of hydrogen by whole numbers. The atomic weight of hydrogen is in the abstract very small, and it would be strange indeed, if this, when multiplied by whole numbers, did not in many cases give a number, within certain limits, approaching (suppose we say of one-fourth or one-eighth of its own atom) those of bodies having higher atomic weights, so that a multiple of the atomic weight of hydrogen could, without introducing an important error, be substituted for that found for other bodies. For instance, by dividing 1351·61, the atomic weight of silver, by 6·2394, the atomic weight of hydrogen, we obtain the number $216\frac{38}{62}$, that is to say, the atomic weight of hydrogen is contained about 216·5 times in that of silver; but even if one-half the atomic weight of the former is added to, or subtracted from, that of a compound of silver, so small a variation is made in the per-centage of that metal, that in many cases 216 may be taken instead of 216·5, the difference only affecting the fourth figure. The error is so small, because the atomic weight of hydrogen is itself very small. An entire misconception of the nature of the investigation respecting chemical equivalents, has led some chemists to permit themselves the license of adding to, or retrenching from, their results so much as the amount of one-half or one fourth of an equivalent of hydrogen, seeing that it altered very little the relation of the numbers to each other, provided it led to whole numbers, which were multiples of the equivalent of hydrogen. It is in this

manner that the number 75 is arrived at as the atomic weight of carbon, that number being very nearly the multiple of the atomic weight of hydrogen, by the whole number 12.

This is doubtless an unusual mode of controlling the accuracy of an experiment, yet the numbers thus modified have been admitted by many chemists.

The fact that the atomic weights of simple bodies are very nearly the multiples of that of hydrogen by whole numbers, is in itself nothing remarkable; there are other numerical relations of this kind, which appear far more extraordinary, on the strength of which, however, no one would think of making a change in atomic weights.

Thus, if we add to the atomic weight of potassium	489·92
the atomic weight of lithium, which is	80·33
we obtain the number	570·25

And this divided by 2, gives 285·12; now this last is as near the atomic weight of sodium, which in chemical properties is a link between the two former bodies, as is the atomic weight of that body obtained by multiplying that of hydrogen by a whole number.

Again, the sum of the atomic weights of barium and of calcium, divided by 2, gives very nearly that of strontium; the sum of those of chlorine and of iodine, divided by 2, gives nearly that of bromine; and those of iron and cobalt, divided by 2, give that of manganese.

There are evidently hidden connexions in these numerical relations, with which we are not acquainted, and to take them as criteria, before they are understood, is obviously inconsistent with the true spirit of philosophy; the same must be admitted with respect to the hypothetical atomic weight of carbon, 75, for the correctness of which, as yet no experience speaks. The early determination of the atomic weight of lead by Berzelius, entirely confirmed as it is by his later experiments in 1830, is in complete contradiction with the correctness of atomic weights as multiples of that of hydrogen.

His memoir on that subject is indeed highly important in reference to our own investigation, and should not be forgotten by chemists. The following is an extract *verbatim* from his memoir*.

"*Further experiments on the Atomic Weight of Lead and its Oxides.*—The reduction of a metallic oxide by means of hydrogen gas, appears so simple an experiment for determining the atomic weight of a metal, that it might be supposed

* Poggendorff's *Annalen*, B. xix. S. 310–315.

the results obtained would enable us to settle the question, whether or not the atomic weight of a metal is a multiple of that of hydrogen; but the nearer we approach to absolute accuracy, the greater are the obstacles we have to overcome in arriving at such a point. Besides, the circumstance that very few bodies submitted to analysis are absolutely free from all impurity, or from the substances from the compounds of which they are separated, introduces a difficulty which is often not less than that of accurately conducting the analysis itself.

"I was of opinion that crystallized nitrate of lead, which is ignited in a platinum crucible until the nitric acid is entirely decomposed, would give perfectly pure oxide of lead; but when this oxide is reduced by means of hydrogen gas, and the metallic lead dissolved in nitric acid, lead-coloured scales, which prove to be metallic platinum, remain behind. It is true the quantity of this residue is very small, but if the result be depended upon up to the last figure, then even the smallest impurity should be avoided. Crucibles of gold and of silver were also employed, but these are oxidized, and combine with the oxide of lead, even when the salt is introduced in small quantities into the crucible previously heated to redness; indeed oxide of lead thus obtained, is impregnated with the foreign metal to a greater extent than when the calcination takes place in a crucible of platinum.

"This induced me to employ carbonate of lead prepared by precipitation, partly from the acetate and partly from the nitrate of lead, by means of the carbonate of soda; and in order to avoid all admixture of the carbonate of soda with the precipitate, an excess of the salt of lead was employed; but notwithstanding this precaution, and the perfect washing of the precipitate, the atomic weight obtained by means of reduction, oscillated in both cases between 1303·5 and 1306·0; and when the metallic lead was heated with pure water, the latter was found to contain carbonate of soda. Carbonate of ammonia employed as the precipitant, is not objectionable on this ground, but, partly because if special care be not taken, it is difficult to obtain that reagent perfectly free from all traces of the hydrochlorate and of the sulphate of ammonia, and also, because during the calcination, the hydrogen of the ammonia may reduce a small quantity of the oxide to the condition of suboxide, which, though not perceptible, nevertheless notably alters the result.

"By the following method I think I succeeded in obtaining perfectly pure oxide of lead. Nitrate of lead is heated to redness in a platinum crucible, until nothing but oxide of lead remains; this is rubbed to powder, and digested in water

with twice its weight of neutral nitrate of lead for some hours; the liquid is then poured off. The oxide is by this means converted into the basic nitrate ($2\,PbO + NO_5$), which is dissolved in boiling water, the solution filtered whilst boiling hot, and then allowed to cool, when fine scaly crystals are deposited. These were collected, washed, pressed into a consistent mass, and dried. The mother liquor of these crystals contains a still more basic salt, which precipitates on mixing it with a solution of the neutral nitrate. The liquid decanted at the commencement of the process, was therefore treated in this manner in these experiments. The last precipitate, which is pulverulent, was thrown upon a filter, and allowed to drain, and, whilst yet moist, the inside of a platinum crucible was coated with it to the extent of half a line in thickness. This coating, when dry, adheres strongly to the crucible. Since this basic salt does not fuse at the temperature required completely to decompose it, there is formed in this way a quantity of oxide of lead, which it is true contains platinum when in contact with the vessel, but the inner portions are quite free from that metal. In the crucible thus lined, the basic salt is laid in single pieces, so that after the calcination is completed, the oxide can be removed without any admixture of that lining the vessel; for the crucible containing the salt is, previous to the calcination, put into a larger one, having a cover, and the whole is then placed in charcoal, and heated to redness, at which temperature the oxide does not fuse. It is very easily known when the salt is entirely decomposed, for it is first converted into minium, which appears almost black when red-hot; the smallest particle of it can therefore be plainly distinguished. After this change is completed, the heat is continued for a full half-hour, and then the crucible is removed. The oxide thus obtained is of a beautiful lemon-yellow colour, and it does not in the least adhere to the coating. It still possesses the glistening appearance of the decomposed scaly crystals. It dissolves in dilute acetic acid without changing the colour of that liquid in the smallest degree, or leaving any residue, which proves that it contains no minium. The solution, moreover, is not rendered turbid by the addition of nitrate of silver.

" When this oxide was dissolved in nitric acid, precipitated by sulphuric acid, the filtered acidulous liquid concentrated, and the excess of sulphuric acid expelled, sulphate of lead remained behind, from which water did not extract any traces of a copper salt, and it was neither coloured nor rendered turbid by caustic ammonia. The lead obtained by reducing

this oxide by means of hydrogen, dissolved in nitric acid, without leaving any residue. The oxide is therefore pure.

" The oxide in masses, not in powder, is introduced into a glass bulb blown upon a barometer tube, and in this it is weighed. In order to expel all moisture, the bulb was heated over a spirit-lamp, until the oxide assumed a dark orange red colour, and a stream of dry air was then passed through it, after which it was allowed to cool. The oxide regains its lemon-yellow colour by this treatment, proving that no minium is found, for which indeed the temperature is not sufficiently high. The oxide prepared in this manner is very little hygroscopic, so that 13 to 14 grammes contain at the utmost from 1·5 to 2 millegr. of moisture.

" The hydrogen gas was evolved from distilled zinc and sulphuric acid, and was, previous to entering the bulb, conducted through a solution of oxide of lead in caustic potass, and also through a tube containing coarsely powdered hydrate of potass. At the commencement of the operation, and until about two-thirds of the oxide were reduced, the temperature was not raised so high as to make the bottom of the bulb red-hot; when this precaution is neglected beyond certain limits, a portion of the oxide of lead combines with the glass, and is not subsequently reduced. It was on this account that the oxide was introduced in masses, which only touched the glass at a few points; free access between the pieces was moreover by this method afforded to the hydrogen. The first effect of the hydrogen gas is to convert the oxide into suboxide, owing to which the masses become of a dark gray colour; their form and size is not otherwise changed, although the temperature is higher than is required for their fusion, supposing them to consist of metallic lead. As soon as the glass begins to be red-hot at the bottom, small globules of lead are seen to form, and the whole is gradually converted into fused metallic lead. Of the portions of oxide of lead which were afterwards analysed, only two were obtained by one and the same operation; all the others were separately prepared, so that a fault in the preparation of the oxide cannot introduce a constant error into all the analyses; this, however, might easily occur if the same specimen of oxide had been employed in all the different analyses.

Nos.	Ox. of Lead in grs.	Lead.	Oxygen.	Atomic Weight of Lead.	Lead.	Oxygen.
					In 100 parts.	
1.	6·6155	6·1410	0·4745	1294·202	92·8275	7·1725
2.	8·0450	7·4675	0·5775	1293·074	92·8222	7·1778
3.	13·1465	12·2045	0·9420	1295·695	92·8346	7·1654
4.	14·1830	13·1650	1·0180	1293·222	92·8224	7·1776
5.	14·4870	13·4480	1·0390	1294·315	92·8201	7·1779
6.	14·6260	13·5775	1·0485	1294·946	92·8314	7·1686
			Mean	1294·259	92·8277	7·1723

"These results, which range about between 1293 and 1296, appear to prove that the atomic weight of lead lies between those two numbers. The mean of these experiments differs so little from the number arrived at in my former ones, namely, 1294·489, that I consider it unnecessary to alter the latter.

"If the atomic weight of hydrogen is 12·5, then the atomic weight of lead, supposing it to be a multiple of that number, is exactly either 1287·5, or 1300; and if either of these numbers be the true one, it appears to me that my results must have oscillated about one of them, instead of which they, as we see, oscillate about a number which lies precisely midway between the above-named."

It may therefore be concluded, that the fact of an atomic number being a multiple of the equivalent of hydrogen is no proof of its exactness.

There are other means of controlling and estimating anew the atomic weight of carbon. The direct method, viz. that of burning a known quantity of pure carbon, and ascertaining the quantity of carbonic acid formed, is but little fitted for the solution of the point in question, since a complex apparatus is required for collecting the gas, a circumstance which lessens the dependence to be placed in such determinations. If, indeed, it be remembered that even in operating on several grammes of carbon, the variations generally amount to from 8 to 10 millegrammes, it will be evident that a complex apparatus offers no security for absolute accuracy. We have therefore selected a different method; an ordinary one, it is true, but which has been hitherto generally acknowledged to be the most certain and the most free from error in analytical chemistry.

We can, for instance, estimate with great certainty the atomic weights of many organic compounds, namely, numerous organic acids, by determining the proportions in which

they combine with oxide of silver, or, what is the same thing, with metallic silver. These organic acids contain several atoms of carbon, combined with oxygen and hydrogen in certain proportions, which can be ascertained with great facility. It is evident, that if the formulæ of these acids are known with certainty, we obtain the sum of the weights of the atoms of carbon, by subtracting the sum of the atoms of oxygen and hydrogen which they contain from the atomic weights of their compounds, as accurately determined by means of their silver salts. The sum of the atoms of carbon thus ascertained, must, if the formerly received number for carbon be correct, be a multiple of it by a whole number, or it must indicate how far that number differs from the true one. There is no substance, the atomic weight of which we believe to be known with greater certainty, and more precisely determined, than that of silver; the continued and important applications of it by Gay-Lussac, in his assay of silver in the wet way; indeed we may say, every one of his experiments on that subject is a fresh proof of its correctness.

With respect to the atomic weight of hydrogen, there is strong reason for thinking it to be rather less than was formerly supposed. In the three last analyses of water by Berzelius and Dulong, the following numbers were obtained:—

	1.	2.	3.
Oxygen	88·942	88·809	88·954
Hydrogen ...	11·058	11·191	11·046
	100·000	100·000	100·000

Supposing the atomic weight of hydrogen to be 6·2398, then the limits of error lie between the numbers 6·3055 and 6·2085. The difference between these numbers is 0·0970, which would either increase the atomic weight of carbon from 76·437 to 76·534, or reduce it to 76·340. If we take the mean, which is 6·2398, for hydrogen, then the limits of error in the determination of the atom of carbon fall in the second decimal place. Such variations result, as we know, from errors of observation.

The method which we have selected, enables us to estimate the atomic weight of carbon in the condition in which it is contained in organic compounds; and it requires only three weighings:—first, that of the vessel in which the salt is burned; secondly, that of the silver salt; and, thirdly, that of the residual silver. In these three weighings no apparatus is changed, and they take place in one and the same porcelain vessel, of which the weight is constant. The height of the

barometer and the proportion of humidity in the atmosphere, exert no influence on this experiment, and the silver which remains behind is not hygroscopic.

The only precaution in these experiments, to which the greatest attention must be directed, is, of course, the rigid purity of the salt, and consequently the entire absence of all hygroscopic water.

It is at all times a difficult task to obtain a chemical compound in a state of absolute purity; to do this in our experiments, was, however, very important, as even the most minute admixture of a foreign substance must increase the found weight of the atom of carbon.

We were soon convinced that there are but few silver salts available in determinations of this kind; most of them are obtained in the form of caseous, or pulverulent precipitates, which enter into combination with a part of the precipitant. The quantity of foreign matter which adheres to these precipitates is so small, that it does not generally render the estimations of atomic weights incorrect, but, as before observed, we are here obliged to avoid every source of fallacy. We selected from those silver salts which are perfectly crystalline, which retain no water when dried at the ordinary temperature, which are not hygroscopic, and which (and this is a character of great importance) do not sputter when heated. The salts employed should moreover leave behind no carburet of silver after calcination.

There are, as stated above, but few silver salts which are not liable to one or other of these sources of error.

The cyanide of silver, for instance, is easily obtained in a pure state, by precipitating the nitrate of that metal by means of hydrocyanic acid; it can even be obtained in large shining tables, by allowing to cool slowly a hot mixture of hydrocyanic acid, with a dilute ammoniacal solution of silver; carefully washing the crystals thus obtained, with solution of ammonia, and drying them at 120° C. By the latter treatment, and even at the ordinary temperature, all the ammonia is got rid of, and the crystals become opake milk-white, without suffering any other change; they are nevertheless in practice not fitted to be employed in our experiment, for they do not appear to be entirely decomposed by heat.

When the cyanide of silver is first heated, it melts without evolving any gas; by increasing the temperature cyanogen is given off, and a basic cyanide is formed; at a certain point beyond this, flame is developed, nitrogen is then evolved, the flame being at the same time as it were extinguished; and fused carburet of silver, of a dull white colour, remains be-

hind, from which the carbon cannot be expelled by subsequent calcination. It is true the carbon burns at the surface of the carburet, leaving a stratum of pure silver, but this protects the inner part from the contact of oxygen; and when this residue is dissolved in dilute nitric acid, a net-work of pure carbon remains.

The behaviour of the benzoate of silver is very similar to that of the cyanide; it is easily obtained perfectly pure, in beautiful shining crystals, which are not hygroscopic; when this salt, to the amount of 7 to 12 grammes, is heated, it melts and is decomposed; but even after being kept at a red heat for twelve hours, a very considerable quantity of carbon is found in the residue of silver.

The oxalate of silver appeared at first to be the most applicable of any in these determinations, but it is almost impossible to obtain it anhydrous, besides which, when heated in large masses, it deflagrates in the same manner as the fulminating mercury. We could, it is true, ascertain its composition by decomposing it, by means of hydrochloric acid, but we consider it important to bring no foreign element into these determinations. In the following experiments, the *acetate*, the *tartrate*, the *racemate*, and the *malate* of silver were employed.

Acetic acid, owing to its volatility, is easily obtained quite pure. We prepared it by decomposing some brilliantly white sugar of lead, which had been frequently recrystallized, in the usual manner, by means of sulphuric acid. The acetic acid thus obtained, which was free from sulphurous acid, was once more rectified over binoxide of manganese in excess. The pure acid was then partly saturated with ammonia, and precipitated by nitrate of silver in the warm. A shining white precipitate was obtained, possessing the form of small laminæ, having a silvery lustre; this was perfectly washed on a filter, dissolved in hot water, the solution filtered, and left to cool in a glass vessel, when at the bottom, at the surface, and on the sides, broad shining needles of acetate of silver, of an inch in length, were formed; these were again washed with pure water, dried in the air, finely powdered in an agate mortar, and exposed to a stream of dry air at 103° C., until the weight remained unaltered.

In each individual analysis, the weighed salt was once more heated in a water-bath for an hour, and then allowed to cool under a bell-glass with concentrated sulphuric acid; after which it was again weighed. It never occurred in our experiments, that the weight was perceptibly altered by this treatment; this precaution was nevertheless uniformly adopted.

The weighings as well as the burnings were conducted in a thin crucible of Meissner porcelain, which was covered by a platinum lid. All our experiments were fortunately performed with the same crucible, the weight of which therefore was controlled whenever weighings were made.

The calcination of the acetate of silver proceeds very easily, without either swelling up or spirting. The salt at first becomes gray, and, on cautiously heating acetic acid, distils off, and then the salt assumes a brown colour; at length, when the odour of the acid is no longer observable, there remains a gray skeleton of silver, which retains the form of the salt burnt. If the heat be now increased, and the lid raised, so as to admit a current of air, a visible glowing is observed throughout the whole mass, and there remains a spongy mass of shining white metallic silver.

After cooling, the crucible with the silver is weighed, heated to redness anew, weighed again, and so on, until not the slightest change of weight is exhibited. The absence of carburet of silver was always particularly demonstrated by dissolving the silver in dilute nitric acid.

The weighings were effected with a balance, which indicated quite distinctly half a millegramme, even when loaded with 20 grammes. The weights (made by Oerthing of Berlin) were carefully compared previously to employment, and were found to exhibit no appreciable variation in their subdivisions. Lastly, we adopted the precaution of conducting one-half of the experiments with newly prepared salt, by which means the fact, that the numbers yielded by salts prepared by different operations agree, is rendered very obvious.

The tartrate of silver is not easily obtained in a crystalline form. When the nitrate of silver is precipitated in the cold by a solution of pure Rochelle salt, from which, by the addition of a little nitric acid, the weak alkaline reaction which it generally possesses has been removed, a caseous and not a crystalline precipitate is formed. On the other hand, if the precipitation is effected by mixing boiling hot and dilute solutions, the liquid becomes brownish, but not turbid, and on cooling, metallic silver in brown laminæ falls down. Again, when a dilute solution of nitrate of silver is heated to from 80° to 85° C., and to this a hot concentrated solution of the tartrate of potass and soda is added, a precipitate falls, which, by agitating, at first disappears; if the addition of the tartrate of potass and soda be discontinued as soon as the precipitate is permanent, and is not redissolved, fine scales of the tartrate of silver separate on cooling, which, after being well washed and dried, are very white, and have a metallic lustre, resem-

bling that of polished silver. In this process the liquid must always contain a slight excess of the nitrate of silver.

The pure tartrate of silver was dried, and its silver determined by means of calcination, observing the same rules of precaution as in the case of the acetate. By gently heating the salt pyrotartaric and carbonic acids distil off, and there remains, without spirting or swelling, a spongy mass of bright metallic silver, which, when washed with water, yielded to it no trace of alkali. Of four determinations which we made, two were with salts prepared by different operations; that employed in the fifth, was prepared with very special care by a gentleman in the laboratory at Giessen, in the course of his investigation on the constitution of organic acids, and with a view to discover, if possible, some difference between the atomic weights of the tartaric and racemic acids. For the preparation of the racemate of silver, very pure racemic acid was half neutralized by ammonia, the resulting sparingly soluble acidulous salt was washed with water, redissolved in water containing ammonia, and again thrown down by means of nitric acid. The acid racemate of ammonia thus obtained was brilliantly white, and perfectly pure. This was employed in the preparation of crystallized racemate of silver, exactly in the manner described for the tartrate of that metal. These two salts do not differ from one another in appearance, but the racemate is less soluble in hot water than the tartrate.

We prepared the malate of silver by means of the acid malate of lime, and nitrate of silver. The acid malate of lime is, by virtue of its very unequal solubility in hot and cold water, easily obtained perfectly pure. Nitrate of silver is mixed with a warm solution of this acid malate, when immediately a granular crystalline, very heavy precipitate falls. Since, after frequently washing this silver salt with water, the fluid still contained traces of lime, the whole precipitate was dissolved in dilute nitric acid, and to this solution ammonia was added drop by drop, taking care that free acid should always be present in excess. The malate of silver is in this case free from lime and ammonia, and is, after continued washing, quite pure.

The malate of silver is decomposed when heated; it fuses, at the same time evolving fumaric acid, carbonic acid, and water, and there remains behind a porous cake of silver, which is free from carbon.

The following are the results of our experiments, represented in a tabular form.

Nos.	Weight of the Salt in Grammes.	Weight of Silver in Grammes.	In 100 Parts.			Atomic Weight of the Salt.	Sum of Four Atoms of Carbon.	Atom of Carbon.
			Silver.	Oxide of Silver.	Acid.			
				Acetate of Silver.				
1.	4·8735	3·1490	64·615	69·396	30·604	2091·790	302·745	75·686
2.	7·5870	4·9030	64·624	69·402	30·598	2091·504	302·458	75·615
3.	6·4520	4·6950	64·623	69·405	30·595	2091·511	302·465	75·616
4.	5·7905	4·7415	64·614	69·395	30·605	2091·804	302·758	75·689
5.	4·1000	2·6490	64·610	69·390	30·610	2091·951	302·905	75·726
	28·803	18·612	64·618	69·399	30·601	2091·680	302·634	75·658
				Tartrate of Silver.				
1.	3·8400	2·2770	59·297	63·684	36·316	2279·390	302·824	75·706
2.	2·7597	1·6365	59·299	63·688	36·312	2279·270	302·704	75·676
3.	3·2356	1·9183	59·287	63·674	36·326	2279·751	303·185	75·799
4.	5·4217	3·2147	59·293	63·682	36·318	2279·530	302·964	75·741
5.	0·9630	0·5710	59·293	63·681	36·319	2279·505	302·939	75·735
	16·220	9·6175	59·294	63·682	36·318	2279·491	302·925	75·731
				Racemate of Silver.				
1.	5·2640	3·1210	59·290	63·676	36·324	2279·670	303·104	75·776
2.	9·2668	5·4945	59·292	63·679	36·321	2279·561	302·994	75·749
3.	4·6730	2·7705	59·287	63·674	36·326	2279·751	303·184	75·796
4.	1·6320	0·9675	59·283	63·670	36·330	2279·920	303·354	75·838
5.	6·5976	3·9113	59·284	63·671	36·329	2279·890	303·325	75·831
	27·4334	16·2648	59·287	63·675	36·325	2279·711	304·145	75·786
				Malate of Silver.				
1.	6·8730	4·2610	61·996	66·583	33·417	2180·141	303·575	75·894
2.	4·2635	2·6440	62·015	66·604	33·396	2179·490	302·924	75·731
3.	4·4305	2·7495	62·059	66·651	33·349	2177·951	301·385	75·346
4.	5·6490	3·5030	62·011	66·599	33·301	2179·621	303·054	75·764
5.	4·6820	2·9015	61·972	66·557	33·443	2181·011	304·444	76·111
	25·898	16·059	62·009	66·597	33·403	2179·707	303·141	75·785

It will be observed on first sight, with respect to the proportion of oxide and of acid in each particular salt, that our results yield the same number up to the third, and in many cases to the fourth figure; and, in our opinion, a better selection of salts could scarcely be made than that which was adopted, for the proportion of oxygen in these four salts is just as unequal as that of the hydrogen; hence if an error had been occasioned by the hydrogen, it could not possibly escape observation.

In the *acetic*, *malic*, *racemic*, and *tartaric* acids, the oxygen is as the numbers 3, 4, 5, and the hydrogen as 4 : 6.

With such coincidence as is exhibited in our analyses, the existence of any foreign admixture in these salts, which could have increased the atomic weight of carbon, cannot be supposed. We have, however, still another direct proof of their correctness, viz. in the results which Berzelius obtained in his analyses of the *tartrate*, and of the *racemate* of lead. These were as follows:—

Tartrate of Lead.

Nos.	Salt.	Oxide of Lead.	In 100 Parts.	
			Oxide of Lead.	Acid.
1.	2·000	1·25449	62·7245	37·2755
2	2·000	1·25434	62·7170	37·2830
3.	2·000	1·25522	62·7610	37·2390
4.	2·8873	1·81212	62·7618	37·2382
Mean	8·8873	5·57617	62·7431	37·2569

Nos.	Atomic Weight of Salt.	Sum of Four Atoms of Carbon.	Atomic Weight of Carbon.
1.	2223·191	303·743	75·936
2.	2223·460	304·012	76·003
3.	2221·904	302·456	75·614
4.	2221·871	302·423	75·606
Mean	2222·531	303·082	75·771

Racemate of Lead.

(Mean of several experiments.)

2·000 of the salt gave 1·2550 oxide of lead, from which we obtain 2222·290 as the atomic weight of the salt, 302·842 as the sum of the four atoms of carbon, and 75·711 as the atomic weight of carbon.

The results of our analyses of the acetates, tartrates, racemates, and malates of silver, give as the mean of five experiments with each, the following proportions:—

	Salt.	Silver.	Atomic Weights	
			of the Salt.	of Carbon.
Acetate of silver . .	28·803	18·612	2091·680	75·658
Tartrate	16·220	9·6175	2279·491	75·731
Racemate	27·4334	16·2648	2279·711	75·786
Malate	25·898	16·0590	2179·707	75·785

If we compare our experiments separately with one another, that is to say, the atomic weight of carbon as deduced from the one salt, with that from the others, we observe that the numbers obtained in the analyses of the same salt, agree more perfectly with one another, than do the mean numbers resulting from the analyses of the different silver salts.

If the experiments themselves be assumed to be perfectly exact, this discrepancy must, from the very nature of things, result from some cause. This cause can be no other than the difference between the specific gravities of the different salts. They were weighed, not *in vacuo*, but in air, and in the proportion of their unequal densities, they must displace unequal volumes of air. All these salts in the above weighings must lose weight, and those which are specifically lighter more than the specifically heavier salts. Dr. Clark, at the meeting of the British Association held at Birmingham in 1839, called attention to the influence which these relations exert on determinations by weight, and corrected the experiments of Berzelius accordingly. It is clear, that in weighing of from one to two grammes of substance, these differences will not affect the relation of numbers, but when 20 or more grammes are weighed, the correction ought not to be neglected.

Such a correction must result from a knowledge of the specific gravities of salts. We determined those of the four salts analysed by us, by taking a known weight of the salt in a saturated solution, and comparing the specific gravity of this liquid with that of pure water.

3·1281 gr. acetate of silver displaced 1 gr. = 1 c. c. water at 15° C. But 1 c. c. of air at that temperature weighs 0·00123 gr. (log. 0·0905137−2); 28·800 gr. acetate of silver displaces therefore 0·0113 gr. atmospheric air. These 28·803 gr. of salt weigh consequently 28·814 gr., but the weight was estimated by means of a brass weight of 28·803 gr., which having the sp. gr. 7·8, displaced 0·00455 gr. of air; that is to say, it lost that weight in air.

The above 28·814 gr. of acetate of silver, weighed therefore 28·8098 gr., and the 18·612 gr. of metallic silver which remains behind after the calcination weighed only 18·6113 grammes.

According to these corrections, 28·8098 gr. of the silver salt, yield 18·6113 gr. of metallic silver.

If we correct in this manner the atomic weights of the tartrate, racemate, and malate of silver, the specific gravities of which are *in vacuo*, respectively = 3·4321, 3·7752, and 4·0016, we obtain the following results:—

	Salt.	Silver.	Atom of Carbon.
			Difference from the mean.
Acetate of silver . .	28·8098	18·6113	75·804 — 0·050
Tartrate of silver .	16·223	9·6171	75·861 + 0·007
Racemate of silver	27·438	16·2641	75·908 + 0·054
Malate of silver. . .	25·9019	16·0596	75·843 — 0·011
	Mean atomic weight of Carbon 75·854		

The discrepancies in the atomic numbers for carbon lie therefore in the fourth figure, or, what is the same thing, in the second decimal place. The atomic weight of carbon is therefore 75·854.

If we multiply the atomic weight of carbon as here given, viz. 75·854, by 1·1026, the specific gravity of oxygen, we obtain as the hypothetical weight of a volume of carbon vapour 0·83636; and if to this we add 2·20520, the weight of 2 volumes of oxygen, and divide the sum of these by 2, we obtain the number 1·521 for the specific gravity of carbonic acid.

The numbers which have been found for the specific gravity of carbonic acid, by means of the direct weighing of the gas, are—

	Sp. gr. of carb. acid.	Calculated at. weight.
By Biot and Arago	1·519	75·530
By Berzelius and Dulong	1·524	76·437
Calculated from our own analyses	1·521	75·854

We consider it as a further proof of the correctness of the atomic weight of carbon as determined by us, that our result lies intermediate between those of the observations of four such distinguished experimenters; and indeed all doubt must be dissipated, when we reflect that with our number the differences observed in organic analyses are legitimately accounted for*.

* Extract of a letter from Berzelius to Professor Wöhler:—

"April 2, 1841.

"Baron Wrede is engaged with experiments in reference to the specific gravity of gases. He has devised peculiar methods of obtaining a balloon of gas in a pure state, which supersede those employed by Dulong and myself. The weights of carbonic acid gas as hitherto determined by him, nearly agree with those of Dulong and myself. He has found, however, that the specific gravity of that gas is not the same under unequal pressures, but that it diminishes with the decreased pressure until one-third of an atmosphere; below this point it is constant. Its specific gravity at the ordinary pressure

IV. *On Malic Acid, and the Changes undergone by its Salts at High Temperatures.* *By* ROBERT HAGEN, *Ph. D.*

Read June 1, 1841.

AFTER the publication of Mr. Graham's observation, that phosphoric acid, in its different states, possesses the property of combining with one, with two, and with three atoms of base respectively, it was discovered by Liebig that the same law holds good in part with many organic acids; some of these acids requiring two, and some three atoms of base, to form neutral salts. The hydrates of each acid contain a corresponding number of atoms of basic water, which cannot be removed without the decomposition of the acids themselves. These chemists showed that, though a salt of any acid, with magnesia or with oxides isomorphous with it, possessed the power of combining with a potash salt of the same acid, and forming a double salt, such as the sulphate of magnesia and potash, that is not ground for doubling the atomic weight of the acid, or for viewing it as bibasic.

They proved at the same time that a monobasic acid is incapable of forming a double salt with two isomorphous bases. The proportion of base which unites with a polybasic acid is constant, generally either two or three atoms. In the memoir on organic acids by Liebig, here alluded to, he had made it not improbable that *malic acid* is bibasic. At his suggestion I have made several analyses of its various salts, which form the subject of this paper.

Malic acid was first discovered by Scheele in the juice of the apple; it was again discovered by Donovan in the juice of several plants, and described by him as a new acid. The identity of the acid of Donovan with malic acid was proved by Braconnot. This acid has been most fully described by Liebig. It has also been partially examined by Pelouze, Braconnot, and Richardson.

The malic acid used in the present investigations was prepared from the expressed juice of the berries of the *Sorbus occuparia*, or Service tree, in the following manner. The expressed juice was mixed in a copper pan with finely divided

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is therefore somewhat too high, and it contains more than one volume of oxygen; thus it is clear that the atomic weight of carbon, as calculated from this, is also too high. That, calculated from his specific gravity, at the pressure of one-third of an atmosphere, is 75·7. He has as yet, however, only made three weighings, which he considers as little more than introductory experiments of practice. I shall be present tomorrow at the fourth determination."

and levigated hydrate of lime, care being taken not to saturate the fluid completely, but to allow it to remain sensibly sour. Being placed on the fire, it was made to boil for some hours, during which time it gave off a peculiar pungent vapour, which strongly affects the eyes. By degrees neutral malate of lime precipitates, and may be removed with a ladle. By continued boiling, more of the salt is obtained. When no more falls, the vessel is removed from the fire, and allowed to cool, when a little more is precipitated. We must take care in the beginning not to saturate the expressed juice entirely with lime, or so much colouring matter falls with the malate of lime, as to render the acid impure. The neutral malate of lime thus obtained, is dissolved in dilute nitric acid (1 part acid to 10 of water), filtered and evaporated; upon cooling, acid malate of lime crystallizes out in perfectly colourless crystals. It must be well washed with cold water, again dissolved in boiling water, and precipitated by acetate of lead. The lead salt is decomposed by sulphuretted hydrogen, and the malic acid obtained pure by evaporation.

Malic acid forms with bases two neutral salts, one of which becomes anhydrous when dried at 100° C., while the other still retains water at that temperature. It possesses decided bibasic properties, and the hitherto received atomic weight is necessarily doubled.

The following salts have been examined:—

Malates of Lime.

a. Neutral anhydrous Malate of Lime.

$$C_8 H_4 O_8 + 2\,Ca\,O, \text{ or } M\,2\,Ca\,O.$$

This salt is obtained by saturating a solution of malic acid with lime water. It is a crystalline powder, perfectly insoluble hot and cold water.

0·489 gramme of this salt gave 0·319 sulphate of lime, or 32·188 per cent. lime. This gives for the atomic weight of the salt the number 2212·40.

		Calculated.	Found.
1 equivalent of Malic Acid	1461·39	67·24	67·81
2 equivalents of Lime . . .	712·04	32·76	32·18

b. Neutral hydrated Malate of Lime.

$$\overline{M}\ 2\,Ca\,O + 5\,aq.$$
$$\overline{M}\ 2\,Ca\,O + 4\,aq.\ (100°\ C.)$$

If acid malate of lime is saturated with potash, soda, or ammonia, and the solution evaporated at a gentle temperature, we obtain instead of a double salt, malate of lime with 5 equivalents of water, in hard shining crystals. When heated

to 100° C. this salt is converted into a porcellanous mass, and is found to have lost one atom of water. At 150° C. it becomes quite anhydrous. Of the salt in its first state of hydration, 0·422 gramme dried at the temperature of the atmosphere, gave 0·2655 sulphate of lime, or 26·113 per cent. lime, which makes the atomic weight of the salt 2725·0, and gives the following composition :—

		Calculated.	Found.
1 eq. Malic Acid	1461·39	53·44	
2 ... Lime . . .	712·04	26·03	26·113
5 ... Water. . .	562·40	20·53	
	2735·83	100·00	

Of the salt dried at 100° :—

(1). 0·6135 gramme gave 0·4045 sulphate of lime = 27·383 per cent. lime; and consequently the atomic weight, 2600·0.

(2). 0·3660 gramme gave sulph. lime, 0·241, or 27·344 per cent. lime.

(3). 0·335 salt, gave 0·353 sulphate lime, and consequently the atomic weight, 2598·28.

These give—

			Calculated.	Found.	
			1.	2.	3.
1 Malic acid	1461·39	56·71			
2 Lime . . .	712·04	27·14	27·38	27·34	27·40
4 Water. . .	449·92	17·15			
	2623·35				

The previous analyses of the lime salt dried without heat, shows the necessity of doubling the atomic weight of the acid, as otherwise we should be obliged to give it the formula

$$C^4 H^2 O^4 Ca O + 2\tfrac{1}{2} aq.;$$

which is at variance with the atomic theory.

Acid Malate of Lime. $\overline{M}$ Ca O H^2 O + 6 aq.

This salt is obtained when neutral malate of lime is dissolved in nitric acid. It crystallizes in large transparent octahedrons. Dried at 100° C. it loses water, and is converted into a viscid, stringy mass.

0·706 salt gave 0·2345 sulphate of lime, or 13·794 per cent. lime; atomic weight, 2585·8.

		Calculated.	Found.
1 atom Malic acid	1461·39	56·10	
1 atom Lime . . .	356·02	13·67	13·79
7 Water	787·36	30·23	
	2604·77		

Richardson and Merydorf concluded the formula of this salt to be, $\overline{M}$ Ca O H^2 O + 8 aq.

Malates of Magnesia.

a. Neutral hydrated Malate of Magnesia.

$\overline{M}$ 2 Mg O + 10 aq
$\overline{M}$ 2 Mg O + 2 aq (100° C.).

This salt is obtained by boiling magnesia in a solution of malic acid, and crystallizing. It loses 8 atoms of water by 100° C.

0·5505 salt gave 0·2708 sulphate of magnesia, equivalent to 16·713 per cent. of magnesia; and makes the atomic weight 3091·4.

		Calculated.	Found.
1 eq.	Malic acid 1461·39	47·09	
2 ...	Magnesia.. 516·70	16·66	16·713
10 ...	Water. . . 1124·8	36·55	
	3102·89		

Of the salt dried at 100° C., 0·466 gave 0·109 sulphate of magnesia, equivalent to 23·390° per cent. magnesia.

		Calculated.	Found.
1 at.	Malic acid 1461·39	66·34	
2 ...	Magnesia. 516·70	23·45	23·39
2 ...	Water . . 224·96	10·21	
	2203·05		

This salt was also analysed by Professor Liebig with the same result.

b. Neutral anhydrous Malate of Magnesia. $\overline{M}$ 2 Mg O.

This salt is obtained by precipitating a saturated solution of the former salt (*a.*) with alcohol, and drying at 100° C.

0·344 salt gave 0·0935 magnesia, equivalent to 26·945 per cent.; atomic weight, 1906·88.

		Calculated.	Found.
1 atom	Malic acid 1461·39	73·83	
2 atoms	Magnesia 516·70	26·12	26·94
	1978·09		

Acid Malate of Magnesia. $\overline{M}$ Mg O H^2 O + 3 aq
$\overline{M}$ Mg O H^2 O + aq (100°).

Obtained by dividing and saturating one half of the malic acid with carbonate of magnesia, and evaporating to crystal-

lization. It loses 2 atoms of water by 100° C.; at a higher temperature it melts.

1·1755 salt gave 0·1405 magnesia, equivalent to 11·952 per cent.; and for the atomic weight, 2161·5.

		Calculated.	Found.
1 atom	Malic acid	1461·39	67·35	
1 ...	Magnesia	258·35	11·91	11·952
4 atoms	Water ...	449·91	20·74	
		2169·66		

Of the salt dried at 100° C., 0·698 gave 0·0795 magnesia, or 13·294 per cent.; atomic weight, 1943·0.

		Calculated.	Found.
1 eq.	Malic acid	1461·39	75·147	
1 ...	Magnesia	258·35	13·285	13·294
2 ...	Water . .	224·96	11·568	
		1944·70		

Malates of Zinc.

a. Neutral Salt.

$$\overline{M}\ 2ZO + 6\,aq$$
$$\overline{M}\ 2ZO + -\ (100°\ C.).$$

Is prepared by digesting carbonate of zinc with malic acid, at a temperature not above 30° C. Dried at 100° C. it becomes anhydrous.

Of this salt, 0·4570 gave 0·2935 sulphate of zinc, or 32·179 oxide of zinc, making the atomic weight 3127·8; the calculated one being 3142·77.

0·695 of the salt dried at 100° C. gave 0·566 sulphate of zinc, or 40·302 oxide of zinc; making the atomic weight 2463·6; the calculated is 2467·6.

Acid Malate of Zinc. $\overline{M}.\ ZOHO + 2\,aq.$

Prepared by adding excess of malic acid to the neutral salt.

0·190 of this salt gave 0·082 sulphate of zinc, or 21·343 per cent. of oxide of zinc; the atomic weight deduced from which is 2351·7. The composition of the salt is therefore—

		Calculated.	Found.
1 eq.	Malic acid . .	1461·4	63·480	
1 ...	Oxide of zinc	503·2	21·861	21·343
3 ...	Water	337·4	14·659	
		2302·0		

Braconnot analysed this salt with the same results.

Basic Malate of Zinc.

If malic acid is long boiled with excess of carbonate of zinc, there falls down a sandy powder; of this salt dried at 100°,

(1.) 0·3935 gave 0·178, or 44·66 per cent. of oxide of zinc; atomic weight, 2253·3.

(2.) 0·255 gave 0·224 sulphate of zinc, or 44·015 per cent. of oxide of zinc; atomic weight, 2286·8.

(1.) 0·474, burnt with oxide of copper, gave 0·1075 water, and 0·329 carbonic acid.

(2.) 0·5510 gave water 0·1335, and 0·3835 carbonic acid. This salt is therefore composed of

	Calculated.		Found.	
12 at. Carbon . . .	917·22	20·19	19·191	19·24
9 ... Hydrogen. .	112·32	2·47	2·52	2·69
15 ... Oxygen . . .	1500·00	33·03	33·62	34·04
4 ... Oxide of zinc	2012·9	44·31	44·66	44·015
	4542·44			

Heated to 100° C. it lost 4 atoms of water; and 0·420 gave 0·411 sulphate of zinc, or 49·082 per cent. oxide of zinc; atomic weight, 2052·3. 0·4225 gave 0·0715 water, and 0·334 carbonic acid, which gives the formula $C^{12}\,H^{5}\,O^{11} + 4\,Z\,O$. This salt, however, is then essentially altered, part of its malic acid being converted into fumaric acid, as will be shown in the sequel.

Acid Malate of Copper. $\overline{M}\,Cu\,O\,H^{2}\,O + 2\,aq$

$\overline{M}\,Cu\,O\,H^{2}\,O$ (100° C.).

Prepared by dissolving hydrated oxide of copper in malic acid, and evaporating at a temperature of 30° to 40° C., as a small blue crystalline body. 0·690 of this salt gave 0·149 oxide, or 21·521 per cent. of oxide of copper; atomic weight, 2302·17.

The composition calculated from this, is as follows:—

		Calculated.	Found.
1 atom Malic acid	1461·39	63·69	
1 ... Oxide of copper	495·70	21·60	21·821
3 atoms Water	337·44	14·71	
	2294·53		

Dried at 100° it loses 2 atoms of water, and its atomic weight becomes 2069·57.

Malate of Silver. $\overline{M}\,2\,Ag\,O$.

0·2877 salt gave 0·1777 silver, or 66·339 per cent. of oxide of silver. Hence

		Calculated.	Found.
1 eq. Malic acid. . .	1461·39	33·48	33·66
2 ... Oxide of silver	2903·21	66·52	66·33
	4361·60		

Malate of Barytes. $\overline{M}$ 2 Ba O + 2 aq
$\overline{M}$ 2 Ba O (100° C.).

A solution of malic acid is saturated with barytes water, and evaporated at a very moderate temperature. The salt found crystallizes. At 30° C. it loses one atom of water; at 100° C. it becomes quite anhydrous.

Of the salt, 0·5575, dried at the ordinary temperature, gave 0·452 sulphate of baryta, or 53·207 per cent. of barytes; which makes the atomic weight 3956·8, the calculated one being 3600·10. The salt dried by 30° C. gave 54·426 per cent. barytes. That dried at 100° C. is composed of 1 atom of malic acid and 2 atoms of barytes.

Malate of Strontian. $\overline{M}$ 2 St O + 3 aq
$\overline{M}$ 2 St O + 2 aq (100° C.).

Fumarate of Oxide of Æthyl.

This æther is formed whenever malic acid is brought into contact with muriatic æther. Malic acid also, when long mixed with absolute alcohol, or with strong fuming hydrochloric acid, is converted into fumaric acid.

This combination, or fumaric æther, is heavier than water, and has a grateful odour, like that of fruit. It is slightly soluble in water, and is therefore better separated from muriatic æther, when mixed with the latter by distillation, than by means of water. By potash, fumaric æther is converted into alcohol and the fumarate of potash. Kept long in contact with ammonia, it is converted into fumaramide. Purified by being distilled over chloride of calcium, 0·3315 æther gave 0·208 water, and 0·669 carbonic acid. Hence

		Calculated.	Found.
8 atoms Carbon . .	611·48	56·29	55·803
6 ... Hydrogen	74·87	6·89	6·97
4 ... Oxygen . .	400·00	36·82	37·22
	1086·35		

Fumaramide. $C^4 H O^2, N H^2$.

This amide is obtained when fumaric æther is left a long time in contact with an excess of caustic ammonia. Its formation is quite analogous to that of oxamide and the other com-

pounds of amide. In cold water and absolute alcohol it is quite insoluble. It is soluble in boiling water, and again precipitates as the water cools. Left long in contact with water, it is completely converted into fumarate of ammonia. Ammonia is disengaged by the fixed alkalies, and a fumarate formed. By distillation it is decomposed into ammonia; a white body, probably maleinic acid, and a residue of charcoal are left.

0·426 of fumaramide gave 0·1335 water, and 0·2780 carbonic acid. By a qualitative determination of the nitrogen, the latter was found to be to the carbonic acid in volume as 1 to 4.

Carbon	42·37	
Hydrogen . . .	5·33	
Nitrogen . . .	24·53	
Oxygen	27·77	
		100·00

This gives—

				Calculated.
4	atoms	Carbon	305·74	42·46
3	...	Hydrogen . . .	37·44	5·19
1	...	Nitrogen . . .	177·04	24·59
2	...	Oxygen	200·00	27·76
			720·22	100·00

Malates at High Temperatures.

If malates of the earths or alkalies are kept for some time at a temperature varying from 250° to 300° C., they are changed into fumarates, water being the only other product. The changes produced are best observed in the following manner. The fumarate produced is dissolved in as small a quantity of boiling water as possible, and a small excess of nitric acid is added to it. The fumaric acid crystallizes from the solution in its peculiar form, possessing all the properties ascribed to it by Pelouze. I have prepared its silver salt to identify it with certainty. 0·2726 acid gave 0·0885 water, and 0·4115 carbonic acid. This gives the following formula for its composition:—

				Calculated.	Found.
4	atoms	Carbon. . .	305·74	41·84	41·73
2	...	Hydrogen	24·95	3·41	3·60
4	...	Oxygen . .	400·00	54·75	54·683
			730·69		

0·3735 of the silver salt gave 0·3205 chloride of silver, or

69·422 oxide of silver; and 0·4270 gave 0·029 water, and 0·224 carbonic acid.

		Calculated.	Found.
4 atoms Carbon	305·74	14·77	14·50
1 atom Hydrogen . . .	12·48	0·60	0·75
3 atoms Oxygen	300·00	14·49	15·31
1 atom Oxide of silver	1451·6	70·14	69·42
	2069·82		

This remarkable change of malic acid salts into those of fumaric acid, appears to me to bear a strong analogy to the formation of the pyro- and metaphosphates, but this is as yet not sufficiently proved by experiment. I have kept a saturated solution of fumaric acid at a boiling temperature for several days without the slightest change in it. And I have also kept a like solution, in a tube hermetically sealed, for a considerable time at a temperature of 250°, under a pressure therefore of nearly 15 atmospheres, without its being altered in any of its properties. Hence fumaric acid does not appear to be reconvertible into malic acid.

V. *Table of the successive Strengths of Pyroxylic Spirit, corresponding to its successive Specific Gravities, with some Introductory Observations.* *By* Andrew Ure, *M.D., F.R.S., &c.*

Read June 1, 1841.

HAVING been professionally employed by an eminent manufacturing chemist, about eighteen months ago, in experimental researches upon the above spirit, the *holzgeist* of the Germans, I found it necessary to construct the following table, in order to ascertain the commercial value of the article at various densities. The principal use of wood-spirit, as extracted by distillation from pyrolignous acid, or from liquid pyrolignite of lime, is for dissolving shell-lac and sandarac into a varnish for stiffening the bodies of hats, and rendering them impervious to water. Hats imbued with this varnish exhale in the hot apartments where the process is conducted the vapours of the wood-spirit very copiously, and thereby occasion a painful irritation to the eyes of the workmen. Some kinds of the spirit are much more injurious to the eyes and the health than others, even when they have all been rectified to apparently the same pitch of purity and strength by the same operations. One purpose of my researches was to discover

the causes of these variations, which affect the comfort of the operatives, and another was to discover the causes of the variations in the solvent qualities of wood-spirit of the same strength by the hydrometer. Having hitherto but partially succeeded in the attainment of these two objects, I shall not occupy the time of the Society at present with an account of the experiments made with that view, but shall reserve them for a future communication.

The researches of Berzelius, Gmelin, Weidmann, Schweitzer, Kane, Liebig, Dumas, and Peligot, concur to prove that the ordinary wood-spirit of commerce, even in its most highly rectified state, is not like spirit of wine, merely an alcoholic liquor more or less diluted with water, but that it consists of different compounds mingled together, and very difficultly separable from each other. Wood-spirit, xylite, and mesite, are three of these liquid compounds usually associated in pyroxylic spirit. When the common wood naphtha of the druggist is distilled three or four times from pulverized unslaked quicklime, by the heat of a water-bath, the oily impurities and water are got rid of, and an anhydrous fluid is obtained which is not liable to become brown on exposure to light, like the ordinary wood naphtha, and which does not become turbid or milky when mixed with water. This purified spirit, however, still acts as painfully almost as the original cruder article, upon the eyes of the hatters, as I ascertained by trial. One mode of separating *wood-spirit* from xylite and mesite, is founded upon the property possessed by wood-spirit, of forming a compound with chloride of calcium not decomposable at the heat of boiling water, while similar compounds with xylite and mesite are decomposable at that temperature. I did not find that pyroxylic spirit was essentially improved as to its employment in the arts, by being rectified by distillation from its combination with chloride of calcium.

Methol is the name which has been given to the oil formed by the action of sulphuric acid upon wood-spirit, xylite, and mesite; and I believe the same oil is generated by the simple combustion of pyroxylic spirit; for I have observed that when the pyroxylic spirit, which has been treated with both quicklime and chloride of calcium, is burned in a platinum capsule till fully one-half be consumed, the residuum becomes oily and opalescent.

The spirit used for the construction of the following table was purified by distillation from pulverized quicklime, and was drawn over with the heat of a water-bath, at such a temperature that its specific gravity at 60° was 0·8136. When

the specific gravity becomes 0·847 by the dissipation of the lighter spirit, the boiling point is 145° Fahr. I believe that a useful criterion of the nature of pyroxylic spirit would be obtained by comparing its boiling temperatures at different degrees of density. To this point I shall also direct my further investigations.

The temperature of the pyroxylic spirit when the specific gravities were taken, was exactly 60° Fahr.

Spec. Grav.	Spirit per cent.	Over proof of Excise scale.	Spec. Grav.	Spirit per cent.	Over proof of Excise scale.
0·8136	100·00				
0·8216	98·00	64·10	0·9032	68·50	13·1
0·8256	96·11	61·10	0·9060	67·56	11·4
0·8320	94·34	58·00	0·9070?	66·66	9·3
0·8384	92·22	55·50	0·9116x	65·00	7·10
0·8418	90·90	52·50	0·9154	63·30	4·20
0·8470	89·30	49·70	0·9184	61·73	2·10
0·8514	87·72	47·40			Under proof.
0·8564	86·20	44·60	0·9218	60·24	0·6
0·8596	84·75	42·20	0·9242	58·82	2·5
0·8642	83·33	39·90	0·9266	57·73	4·0
0·8674	82·00	37·10	0·9296	56·18	7·00
0·8712	80·64	35·00	0·9344	53·70	11·00
0·8742	79·36	32·70	0·9386	51·54	15·30
0·8784	78·13	30 00	0·9414	50·00	17·80
0·8820	77·00	27·90	0·9448	47·62	20·80
0·8842	75·76	26·00	0·9484	46·00	25·10
0·8876	74·63	24·30	0·9518	43·48	28·80
0·8918	73·53	22·20	0·9540	41·66	31·90
0·8930	72·46	20·60	0·9564	40·00	34·20
0·8950	71·43	18·30	0·9584	38·46	35·60
0·8984	70·42	16·60	0·9600	37·11	38·1
0·9008	69·44	15·3	0·9620	55·71	40·6

VI. *On the Ferrocyanides.* *By* R. Corbett Campbell. *Communicated by Dr.* Clark.

Read June 1, 1841.

IT is well known that the yellow prussiate of potash, heated by itself in close vessels, is decomposed into cyanide of potassium, carburet of iron, and nitrogen gas. I have observed that, heated in contact with the air, the products of the decomposition are very different. The cyanide of potassium takes oxygen from the air, and is thereby converted into cyanate of potash, while the cyanide of iron is decomposed, converting the iron into an oxide. The absorption of oxygen is caused by the presence of the cyanide of iron, for cyanide of

potassium, heated by itself in contact with the air, does not become changed into cyanate of potash. I believe that a process for cyanate of potash may be founded on the above observation, preferable to the common one with oxide of manganese; for it has been proved that this oxide is not essential in the process, and it not unfrequently happens that a large quantity of the cyanide of potassium is converted into carbonate of potash. Sometimes also a little manganese dissolves along with the cyanate.

For the preparation of this salt, then, without the use of manganese, the powdered and dried prussiate of potash is heated almost to redness, in a flat iron vessel, with constant stirring of the melted mass. Some ammonia is evolved, which results from the action of the moisture of the air, for the substance itself contains no hydrogen. The melted mass should be taken out with an iron spatula, allowed to cool, reduced to powder, and again fused; because the melting cyanate of potash is apt to protect little bits of the yellow prussiate from the action of the air. If the heating be properly conducted, not a particle of cyanide of potassium will be formed. The cyanate of potash is dissolved out with hot alcohol filtered and crystallized. The undecomposed prussiate of potash remains undissolved.

The double salt of ferroprussiate of potash and lime acts under heat exactly like the ferroprussiate of potash itself. Well dried and set on fire, it continues to burn, until the alkaline and earthy cyanides are converted into cyanates, and the iron into oxide. The reason that the double salt continues to burn is to be found in the porous state of the mass, which offers no obstacle to the free access of air; whereas the yellow prussiate alone fuses, and prevents the progress of the combustion.

The ferrocyanide of zinc, which always contains some ferroprussiate of potash in chemical combination, likewise continues to burn, and affords cyanate of potash and the oxides of the metals.

When the double salt of potash and lime is heated in the air as above mentioned, and then dissolved in water, the solution possesses the remarkable property of becoming pink in the sun's rays, and again becoming colourless in darkness. Neither cyanate of lime nor cyanate of potash, together or singly, or mixed with prussiate of potash, show this reaction. It is hence probable that this solution owes the above-mentioned property to the admixture of some foreign substance, present probably in a very small quantity. All attempts to isolate any such substance were fruitless.

As the shade of colour in the above solution is exactly that of a solution of permanganate of potash, the solution and the substances used were tested for manganese. They contained none. The reactions of this solution too stand in contradiction with some of those of the permanganates. The presence of ferrocyanide of potassium is essential to the production of the pink in the sun's rays, but the action of the same salt on permanganate of potash is first to reduce it to the green manganate, and by further addition of the prussiate to oxide of manganese. As the prussiate of potash of commerce often contains traces of sulphocyanide of potassium, the experiments were repeated with prussiate of potash, that had been washed with hot alcohol, and by this means all sulphocyanide removed; but no difference was observed in the result.

It is further clear, that this salt, even if it were present in the prussiate of potash, could take no part in the above-mentioned reaction, for it gives no precipitate with a lime salt, with or without the presence of prussiate of potash. An alkaline state of the liquid is essential to the production of the pink in the sun's rays; so is likewise the presence of a ferrocyanide. If a solution of nitrate of copper be added to a solution of the heated double salt, till all ferrocyanide be removed, and then the excess of copper precipitated by carbonate of potash, the solution will have lost entirely the property of becoming coloured in the sun's rays, but will recover it on the addition of a few drops of a solution of yellow prussiate of potash.

The air exercises no influence on these changes; they take place equally distinctly in closed vessels.

A temperature of 120° Fahr. destroys the colour, but on cooling and re-exposure to the sun's rays, the colour again appears. By evaporation in the rays of the sun, a pink salt is obtained. The presence of cyanate of potash is not essential to the production of the colour; if muriatic acid be added to the solution until all cyanic acid be destroyed or removed, and then supersaturated with alkali, the solution possesses the colouring property as strong as before. Another proof that cyanate of potash is not essential, is that the double salt of ferroprussiate of lime and potash heated in closed vessels, and dissolved in water, shows likewise the same reaction, although containing no cyanate of potash.

I have already stated, that the investigation undertaken with the view of isolating the colouring substance in these experiments, was without success; nevertheless some observations were made which seem to stand in relation to this subject.

It has often been remarked, that, on adding an acid to the solution of the heated double salt, a minute quantity of a reddish powder is precipitated. This powder contains iron; it is decolorized by carbonate of potash, but the colour is not reproduced by exposure to the sun. The solution from which this powder has been precipitated, on being saturated with alkali, and exposed to the sun's rays, is found not to have lost the colouring property. I suspect that this red powder is the same as is observed to be precipitated from some specimens of commercial prussiate of potash, on the addition of strong acetic acid. Prussiate of potash is sometimes observed in commerce of a darker tint than usual, and it is this variety which frequently shows the above-mentioned reaction.

If a solution of cyanide of ammonium be added to a solution of acetate of copper, a compound of copper and cyanogen is precipitated, not analogous in its composition to the cyanide from which it is precipitated. The supernatant solution becomes pink-coloured for a few seconds. In order to see if this reaction result from the action of the free cyanogen on the cyanide of ammonium, a stream of this gas was sent through a solution of the salt. It became first yellow, and then red, but a different red from that mentioned in the reaction with the copper salt.

Professor Liebig pointed out to me another instance of a fugitive pink colour occurring in a cyanogen compound, which Prof. Gmelin of Heidelberg has mentioned in his System of Chemistry. When strong nitric acid is added to pounded yellow prussiate of potash, and slightly heated, much cyanogen gas is evolved; when the heat is not too strongly applied, neither prussic acid nor nitrous acid are remarked. The mass becomes black, and is quite soluble in water: if there be added to this solution, first, an excess of potash, and then some drops of sulphuret of potassium, the solution becomes beautifully pink-coloured, disappearing after the lapse of a few seconds.

It differs from the pink colour observed as occurring in the solution of the heated double salt when exposed to the sun, in its action to sulphuretted hydrogen. This gas, or an alkaline sulphuret, instantly destroys the colour resulting from the action of light, while an alkaline sulphuret is essential to the production of the other. The pink colour of the solution to which sulphuret of potassium has been added, becomes soon purple, and afterwards deposits a blue substance, which long kept in the solution becomes white. This blue precipitate cannot be prussian blue, for it is produced in an alkaline solution, and is instantly decolorized by acids. It is possible that

the above pink solution owes its colour to the same substance as is present in Gregory's solution of sulphuret of azote in caustic potash.

I have brought forward these different instances of coloration occurring in cyanogen compounds, because they seem to point out the existence of a yet unexamined class of prussiates.

On the Acid Cyanurate of Potash.

Mineral acids, as well as acetic acid, were found to have the power of converting the neutral cyanate of potash into the acid cyanurate. The essential circumstance in this process is that the solution of the cyanate of potash be concentrated. The process above described for making cyanate of potash by calcining in the air the yellow prussiate of potash, affords a ready means of making this salt easily, and in quantity. The roasted prussiate is digested with cold water, filtered, and muriatic acid, added to the precipitated salt, is dissolved in hot water, and crystallized by cooling.

The foregoing experiments were partly confirmed and partly originally performed in the laboratory at Giessen, in 1838.

This paper is the only scientific memorial of its amiable author, who died about two years ago, at an early age, but mature enough to have endeared him to many men of science, and to have indicated promise of scientific eminence. He will be most remembered by his friends for a marked rectitude of mind, combined with an uncommon ardour; evincing itself in the warmth of kindly feelings and in the enthusiasm of scientific pursuits.—T. C.

VII. *Examination of Cetine, Ethal, Oils of Laurel Turpentine, Hyssop, and Assafœtida.* By Dr. JOHN STENHOUSE.

Read November 17th, 1841.

Cetine.

CHEVREUL gave the name of Cetine to spermaceti when rendered absolutely pure. The spermaceti of commerce always contains more or less of a yellowish oil, which it retains with great tenacity, and by which its melting point is greatly lowered. The best means of purifying spermaceti, is to treat it two or three times with boiling alcohol, in which, however, it is very slightly soluble, and then to subject it to nine or ten crystallizations in æther. These solutions and crystallizations must be repeated till the temperature at which the cetine solidifies reaches 120° F. or 121° F., when it may be regarded as perfectly pure.

The cetine which I subjected to analysis, was prepared in the manner just described, and solidifies at 121° F. The following are the results:—

(1.) 0·236 gramme gave 0·6805 carbonic acid, and 0·2831 water.

(2.) 0·3198 gramme gave 0·9223 carbonic acid, and 0·378 water.

(3.) 0·2533 gramme gave 0·7286 carbonic acid, and 0·3008 water.

(4.) 0·2928 gramme gave 0·8468 carbonic acid, and 0·3476 water.

	1.	2.	3.	4.
Carbon	79·72	79·74	79·53	79·96
Hydrogen	13·32	13·13	13·19	13·19
Oxygen	6·96	7·13	7·28	6·85
	100·00	100·00	100·00	100·00

These analyses differ considerably from that of Chevreul, though I have repeated them with every attention to accuracy. Chevreul found

Carbon	81·660
Hydrogen . . .	12·862
Oxygen	5·578
	100·000

It is needless, however, at present attempting to deduce any formula from these analyses, as the acids which spermaceti contains have not been accurately determined. Spermaceti is usually supposed to consist of margarate and oleate of ethal. From experiments, I have reason to think that one of them is margaric acid, but as spermaceti, when distilled, yields no

trace of sebacic acid, there is every reason to conclude the other acid it contains, the quantity of which is extremely small, is certainly not the oleic acid.

In order to ascertain how far cetine differs in composition from ordinary spermaceti, I was induced to submit a portion of the latter also to analysis. The melting point of the crude spermaceti analysed was only 107° F.

(1.) 0·3279 gave 0·9499 carbonic acid, and 0·3904 water.
(2.) 0·349 gave 1·0065 carbonic acid.
(3.) 0·3755 gave 1·0887 carbonic acid, and 0·4399 water.

	1.	2.	3.
Carbon	80·10	79·74	80·16
Hydrogen . . .	13·23		13·01
Oxygen	6·67		6·83
	100·00		100·00

It is evident from these analyses, that the composition of crude spermaceti is precisely the same with that of the purest cetine. The small quantity of oil, therefore, which accompanies the former is probably isomeric with the more solid fat.

Ethal.

The ethal which I analysed was prepared by saponifying spermaceti with powdered potash. The saponification was twice repeated, in order that none of the spermaceti might escape decomposition. The lime-soap was then formed by precipitation with chloride of calcium. It was dried with a gentle heat and the ethal extracted by æther: alcohol was found inadmissible, as a large quantity of the lime-soap was also dissolved by it. I also found it advantageous to mix the lime soap with a considerable quantity of pounded glass, as this prevented its adhering to the sides and bottom of the vessel when heated, and thus enabled the æther to act more equally on every part of the mass. The ethal first obtained was again boiled with milk of lime, again extracted with æther, and repeatedly crystallized. Its melting point was 119° F.

(1.) 0·5307 gave 1·519 carbonic acid, and 0·665 water.
(2.) 0·2881 gave 0·8295 carbonic acid, and 0·361 water.
(3.) 0·302 gave 0·8645 carbonic acid, and 0·383 water.

	1.	2.	3.
Carbon . . .	79·14	79·61	79·15
Hydrogen . .	13·92	13·02	14·08
Oxygen . . .	6·94	6·47	6·77
	100·00	100·00	100·00

These analyses agree very closely with the calculated numbers, and with the analyses of Chevreul and Dumas.

	Calculated numbers. Atoms.	Per cent.
Carbon	32 =	79·69
Hydrogen.	34 =	13·82
Oxygen	2 =	6·51

Laurel Turpentine.

For some years past an essential oil, to which the name of Laurel has been improperly given, has been imported in considerable quantities from Demerara and some other parts of South America. It has been successfully employed as an external application for the cure of rheumatism. It is also an excellent solvent for caoutchouc, as it dissolves that substance very readily, and leaves it in a firmer and less altered state than either naphtha or oil of turpentine. Its comparatively high price, however, 1*s.* per oz., precludes its employment for this purpose. The botanical nature of the tree which produces it is unknown. The Spaniards call the tree "acaita de sassefras." I think it probable that it is a species of pine. These trees are not very abundant, but the quantity of oil they contain is exceedingly great. It runs out abundantly when incisions are made near the root of the tree, and it also not unfrequently exudes spontaneously. The oil as it occurs in commerce is transparent, but of a slightly yellow colour, owing to its containing a little resinous matter, which is easily removed by distilling it with water. The smell of this oil reminds one of that of turpentine, but it is much more agreeable, and approaches more nearly that of oil of lemons; its specific gravity is 0·8645 at 56° F. Oil of laurel is accompanied with a volatile acid, the quantity of which, however, is extremely small. When this acid is boiled with nitrate of silver, the oxide is reduced to the metallic state. The acid is probably therefore the Formic.

To prepare the oil for analysis it was distilled with water to remove the resin it contained, and then rendered anhydrous by fused chloride of calcium. When rectified on the oil-bath, it began to boil at 301° F., but the boiling point gradually rose to 325° F. It was then transparent and colourless. The first portion that distilled over was set aside, but the second and third, which contained nearly an ounce each, were separately collected, and subjected to analysis with oxide of copper.

(1.) 0·2677 gramme, boiling at 301° F., gave 0·857 carbonic acid, and 0·279 water.

(2.) 0·2839 gramme, boiling at 325° F., gave 0·9062 carbonic acid, and 0·2956 water.

	1.	2.	Calculated numbers. Atoms.
Carbon.	88·51	88·29	88·46 = 5
Hydrogen . . .	11·57	11·57	11·54 = 4
	100·08	99·83	100·00

It is evident from these analyses, that oil of laurel consists of two or more isomeric oils belonging to the numerous tribe of carburetted hydrogens of which oil of turpentine is the type, containing carbon and hydrogen in the proportion of 5 to 4. The action of the reagents on oil of laurel is so similar to that on oil of turpentine as to render details unnecessary. The reason which has induced me to change the name of oil of laurel to that of laurel turpentine is, that there are two oils of laurel already, one fixed and the other volatile, with which it might otherwise be easily confounded.

Oil of Hyssop.

The essential oil of hyssop is easily obtained by the usual process of distilling the plant with water. The quantity which it yields is pretty considerable. The oil has the smell of the plant, and its taste, like that of the other essential oils, is very pungent. When fresh it is transparent and colourless, but when kept some time, especially if the air is not carefully excluded, it becomes yellowish, owing to the formation of a small quantity of resin. Oil of hyssop is lighter than water and quite neutral; its boiling point is not at all fixed; it begins to boil at 288° F., but the boiling gradually rises till it reaches 325°, soon after which it begins to pass over coloured: it is evidently a mixture of several oils. In order to determine this more certainly, the anhydrous oil was rectified, and the product of its distillation at different temperatures collected separately and subjected to analysis. The following are the results:—

1.) 0·289 gramme, boiling at 288° F., gave 0·8794 carbonic acid, and 0·2875 water.

(2.) 0·3022 gramme, boiling at 299° F., gave 0·8885 carbonic acid, and 0·298 water.

(3.) 0·2838 gramme, boiling at 335° F., gave 0·8243 carbonic acid, and 0·2671 water.

	1.	2.	3.
Carbon	84·13	81·29	80·31
Hydrogen. . .	11·05	10·95	10·45
Oxygen.	4·82	7·76	9·24
	100·00	100·00	100·00

It will at once be perceived from these results, that the por-

tion of the oil richest in carbon and hydrogen distils over at a comparatively low temperature, and that as the quantity of oxygen in the oil increases, its boiling point rises. This is what usually takes place with oils which consist of a mixture of a carburetted hydrogen, and more or less oxygenated oils. I was induced therefore to try if these different oils could be separated by treating them with fused potash—the method so successfully employed by Messrs. Gerhardt and Cahours with oil of cumin, and which promises to be extremely useful in the investigation of this class of bodies. The oil of hyssop was dropped upon the potash through a capillary opening in the tubes of a retort. As soon as the oil came in contact with the melted potash, the greater portion of it was converted into a brownish resin, but a part of it passed into the receiver. This portion was again subjected to the action of the potash, when still more of it was converted into resin. What distilled over was considerably different in taste and smell from ordinary oil of hyssop. When subjected to analysis,

0·3047 gramme gave 0·955 carbonic acid, and 0·313 water, =

Carbon	86·65
Hydrogen.	11·41
Oxygen	1·94
	100·00

It is evident, therefore, that I did not succeed in converting oil of hyssop into a pure carburetted hydrogen, though the quantity of the oxygenated oil was considerably diminished.

Oil of Assafœtida.

It is to this oil that assafœtida owes its highly offensive smell. The quantity of oil which the resin yields, varies according to its freshness. A pound of the resin generally yields about one-third of an ounce of oil, which is obtained by distillation with water in the usual way. It is advisable to mix the resin with pounded glass, as this prevents the resin from adhering to the bottom of the retort, and both hinders it from burning and diminishes the violence of the succussions with which the distillation would otherwise be attended. The oil has usually a slightly yellowish tint: its specific gravity is 0·9428 at 60° F.; its taste is first mild and then acrid. When exposed for some time to the air it oxidizes, and a resinous matter forms in it. In order to prepare it for analysis, the oil which had been twice distilled with water to remove all the resin was rectified over chloride of calcium on the oil-bath. Its boiling point is by no means constant; it began to boil at 325° F., and continued to rise till it reached 370° F. The receiver was changed three times during the distillation, and the

products separately collected and analysed. The presence of sulphur in oil of assafœtida was first noticed by Zeise. It differs from oil of mustard, by containing no nitrogen. The carbon and hydrogen were estimated by analysis with oxide of copper, and the sulphur was determined by passing the oil in vapour over a mixture of nitre and carbonate of baryta at a red heat. The following are the results:—

(1.) Analysis of 1st quantity, 0·2967 oil, boiling at 325° F., gave 0·710 carbonic acid, and 0·2625 water.

(2.) Analysis of 1st quantity, 0·2915, gave 0·6935 carbonic acid, and 0·253 water.

Per cent.

0·382 oil gave 0·635 sulphate of baryta = 22·93 sulphur.

0·391 oil gave 0·639 sulphate of baryta = 22·54 sulphur.

	1.	2.
Carbon	66·16	65·78
Hydrogen . .	9·83	9·64
Sulphur . . .	22·93	22·54
Oxygen . . .	1·08	2·04
	100·00	100·00

(1.) Analysis of 2nd quantity of oil, boiling at 341° F., 0·2312 gave 0·523 carbonic acid, and 0·1967 water.

(2.) Analysis of 2nd quantity, 0·2728 gave 0·6177 carbonic acid, and 0·2224 water.

(3.) Analysis of 2nd quantity, 0·2889 gave 0·6461 carbonic acid, and 0·2447 water.

0·413 oil gave 0·601 sulphate of baryta = 20·12 per cent. sulphur.

0·421 gave 0·610 sulphate of baryta = 19·99 per cent. sulphur.

	1.	2.	3.
Carbon.	62·54	62·60	61·83
Hydrogen . . .	9·45	9·05	9·41
Sulphur	20·12	19·99	
Oxygen	7·89	8·36	
	100·00	100·00	

(1.) Analysis of 3rd quantity of oil, boiling at 370° F., 0·3036 gave 0·6415 carbonic acid, and 0·2493 water.

(2.) Analysis of 3rd quantity of oil, 0·2947 gave 0·6185 carbonic acid, and 0·2413 water.

0·344 gave 0·421 sulphate of baryta = 16·88 per cent. sulphur.

0·382 gave 0·436 sulphate of baryta = 15·74 per cent. sulphur.

	1.	2.
Carbon.	58·42	58·03
Hydrogen . . .	9·12	9·09
Sulphur	16·88	15·74
Oxygen	15·58	17·14
	100·00	100·00

It is evident from these results, that oil of assafœtida is a mixture of various oils, one or more of which consist probably only of carbon, hydrogen and sulphur, with other oils containing more or less oxygen. The less oxygenated portion is the most volatile. It is therefore unnecessary to attempt to deduce any formula from these analyses. Though oil of assafœtida was twice treated with fused potash in the same manner as oil of hyssop, the greater portion of the sulphur was removed, but I could not succeed in getting rid of the whole. The greater portion of the oil was converted into a blackish resin. This resinous matter is soluble in alkali, from which it is precipitated by acids. It is not in the least degree crystalline. The action of reagents on oil of assafœtida was as follows:—salts of silver, lead and protoxide of mercury gave black precipitates. When brought in contact with peroxide of mercury, heat was evolved, and a part of the oxide was converted into a greenish yellow mass, which was insoluble in water. A very small portion of the oil was acted on however. Corrosive sublimate immediately produced a copious flocculent white precipitate. It was insoluble in water, alcohol and æther. It was soluble in nitric acid, and when boiled with solution of potash, the mercury was precipitated in the state of protoxide. Oil of assafœtida does not combine with ammonia. It is very little acted on either by aqueous or alcoholic solutions of potash. Nitric acid acts on this oil with great energy, and the evolution of deutoxide of azote. It is converted into a resin, and on adding a salt of baryta an abundant precipitate of sulphate of baryta is obtained. Sulphuric acid first reddens, and with the assistance of heat, chars it. It dissolves iodine readily, but without explosion.

Glasgow, 14th October, 1841.

VIII. *On the Radical of the Cacodyl Series of Compounds.* By *Professor* BUNSEN *of Marburg.*

Read December 21, 1841.

1. *Isolation of Cacodyl.*

SOME of the cacodyl compounds have the remarkable property of being decomposed by metals. When sulphuret

of cacodyl is heated in contact with mercury in a large vessel to 200° or 300° C., the mercury becomes covered with a stratum of sulphuret of mercury, without any apparent disengagement of gas. The fluid which condenses in the vessel gives off fumes and takes fire of itself in air, if the heat has been continued long enough, and the temperature sufficiently high. This process is, however, not available for the exhibition of cacodyl, as the mercury only acts upon the sulphur compound of cacodyl at a temperature at which cacodyl already begins to be decomposed. Bromide of cacodyl behaves in the same manner; under similar circumstances a mixture of bromide of mercury, and a fluid which fumes in the air, is produced:—

$$\left.\begin{matrix}\mathrm{Kd\ Br}\\ \mathrm{Hg}\end{matrix}\right\} = \left\{\begin{matrix}\mathrm{Kd}\\ \mathrm{Hg\ Br.}\end{matrix}\right.$$

When this mixture is boiled in water, the bromide of mercury is reduced, and bromide of cacodyl is regenerated and given off with the watery vapour:—

$$\left.\begin{matrix}\mathrm{Kd}\\ \mathrm{Hg\ Br}\\ \mathrm{H\ O}\end{matrix}\right\} = \left\{\begin{matrix}\mathrm{Kd\ Br}\\ \mathrm{Hg}\\ \mathrm{H\ O.}\end{matrix}\right.$$

The last reduction also takes place at too high a temperature for the exhibition of the radical. The isolation is most easily and perfectly effected by using a metal capable of decomposing water and forming a chloride, particularly zinc, iron or tin. When tin, or any of the foregoing metals, is added to anhydrous chloride of cacodyl, the metal is dissolved at a temperature of 90° to 100° C., without any evolution of gas. The solution, which is at first clear, becomes of a dark colour on further solution of the metal. Water separates the pure chloride of tin, and leaves cacodyl mixed with a trace of chloride of cacodyl behind:—

$$\left.\begin{matrix}\mathrm{Kd\ Cl}\\ \mathrm{Sn}\end{matrix}\right\} = \left\{\begin{matrix}\mathrm{Kd}\\ \mathrm{Sn\ Cl.}\end{matrix}\right.$$

As zinc, however, effects the reduction of the chloride with the greatest facility, and as no further decomposition takes place in the chloride of zinc formed, I have in my experiments exclusively used this metal for the isolation of the radical.

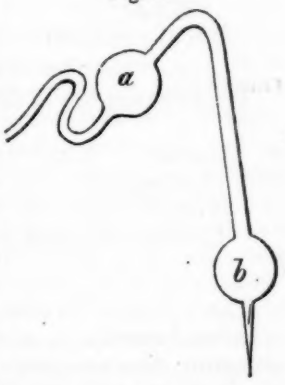
Notwithstanding that the reduction appears so easy, still, as it is very difficult to prevent subsequent decomposition in repeating the distillation and crystallisation of a substance which is as inflammable as the vapour of phosphorus, I think it necessary to enter into further details regarding the method of producing it.

Very thin sheet zinc, the surface of which has been pre-

viously cleaned with dilute sulphuric acid and afterwards well washed, is cut into small pieces, to be employed for this purpose. The chloride of cacodyl must be quite free from oxygen. By digesting oxide of cacodyl three times over in concentrated hydrochloric acid, a pure substance is procured, which does not give off any vapour. This chloride must be allowed to remain in a close vessel with chloride of calcium and caustic potash, without being distilled, in order to deprive it of any water it may contain, and also of any excess of acid. To prevent all access of air in this operation, a glass vessel of this description is employed (fig. 1.). At the opening *a*, a stream of carbonic acid is conducted through the vessel with the bulb *c*, to contain the substance to be dried. When the atmospheric air is entirely displaced, both ends, *a* and *b*, are sealed. When the vessel is required for use, the point *a* is broken and attached by a caoutchouc tube connected to an air-pump; the point *b* is then broken and put under the surface of the chloride of cacodyl; the latter is sucked up into the apparatus, and then immediately closed: I will call this the drying apparatus. The reduction and distillation is carried on, in a somewhat similar manner, in an atmosphere of carbonic acid, in a closed vessel (fig. 2.), the bulb *a* being the distillation tube, and the bulb *b* the receiver.

Fig. 1.

Fig. 2.



The whole apparatus being previously filled with carbonic acid, the chloride of cacodyl is sucked into the bulb *a*, also containing the zinc. The open end of the vessel is then immediately closed with the blowpipe. It is exposed to the temperature of 100° C. for three hours, in a water-bath. The zinc is readily dissolved without any evolution of gas, and the solution becomes of a dark colour. On cooling to 50° C. large cubic crystals are formed, which are redissolved by heating. These crystals are probably a combination of chloride of zinc and chloride of cacodyl. When the zinc is no longer acted upon at 103° C., the contents of the bulbs appear converted into a dry mass of salts, which, upon an increase of temperature to 110° or 120° C., melts into an oily-like

liquid. After the whole apparatus is warmed, the point of the receiver *b* is opened under cold water previously boiled. Upon the entrance of the water, upon the cooling of the apparatus, it is again sealed, and the water is conducted into the distillation bulbs. After a short digestion, a solution of chloride of zinc is formed, the zinc in excess remaining with a clear surface, and leaving the radical at the bottom as an oily liquid. This liquid is then transferred into the drying apparatus, and when perfectly dry is sucked up again into the distilling apparatus, and digested for a short time with clear zinc, by which means a small quantity of chloride of zinc is formed. It is then distilled, and comes over as clear as water. At a temperature of —6° C. large prismatic shining crystals are formed. After two-thirds of the solution has crystallized, the remaining solution is again distilled, and this is repeated three times over. The solution is finally put into a tube filled with carbonic acid.

The analysis of this liquid was conducted in the usual manner with oxide of copper. The arsenic sublimed in fine crystals in the back part of the tube without the formation of any arsenical copper or any arsenical salts. The quantity of arsenic was ascertained by weighing the tube before and after heating.

The analysis gave the following results:—

	1.	2.
Substance	0·620 gr.	0·500 gr.
Carbonic acid	0·500	0·402
Water	0·306	0·200
Tube before heating.	62·681	60·670
... after heating .	61·869	60·020

The composition of this radical is therefore

		Calculated.	1.	2.
Carbon	4 equivalents	23·15	22·30	22·23
Hydrogen	6 ...	5·67	5·48	5·33
Arsenic	2 ...	71·18	71·29	71·
Loss and Oxygen . . .		0·00	0·93	1·44
		100·	100·	100·

The trifling difference between the quantities found and the calculated quantities, arises probably from the impossibility of obtaining this compound free from oxygen. If the results obtained are reckoned in the 100 parts, without taking notice of the oxygen, the carbon and the hydrogen agree still closer. The quantity of arsenic on the contrary appears rather too much. The facility with which cacodyl can be separated from its compounds by simple substances, renders it very

probable that the oxide might be also reduced by means of carbon as well as hydrogen, upon the application of a higher temperature. Dumas's analysis, as well as my previous one, of the liquor of Cadet, renders this supposition nearly certain, and fully explains the cause of our arriving at different results. Dumas found, as I did also, in my first experiments, a constant excess of arsenic, carbon, and hydrogen, which is accounted for by the impurity of the oxide of cacodyl.

There was no difficulty in ascertaining the density of the vapour of the liquid, as the temperature at which it is decomposed is considerably higher than its boiling point.

Substance	0·2500 gramme.
Volume measured	55·98 Cbr.
Temperature	200° C.
Barometer	328·5 lines.
Column of oil	38 lines.
Col. of merc. at 200° C.	44·5 lines.

This gives the density of 7·101, which agrees as nearly as could be expected with the calculated density, viz.—

4	volumes of	vapour of carbon .	3·371
12	...	hydrogen	0·825
2	...	vapour of arsenic .	10·367
			14·563 ÷ 2 = 7·281.

The difference of 0·18 in the result obtained is fully accounted for by the tension of the mercury vapour in the barometer at the temperature of 200° C.

The agreement of both the analysis and density of the vapour with the respective calculated quantities is a matter of considerable interest. Berzelius has shown that when a certain density of a gaseous organical radical is assumed, the relative condensation which the compounds of this radical present, exactly agree with those of inorganic or simple radicals. This circumstance has given a weight to the theory of the compound radicals which the law of substitution could not reach. But this, in connexion with the phænomena of substitutions, does not advance the idea of organic radicals beyond the limits of a hypothesis. The proof of their reality is connected with three other conditions, viz. on their isolation, on the direct formation of their compounds, and on the actual agreement of the density of their simple elements with their theoretical density. All these conditions are fulfilled in regard to cacodyl: it may be isolated, it enters into direct combinations, and it has the density required if the laws of condensation of the inorganic elements are valid for organic bodies, as may be observed by the following statement.

		Observed.	Calculated.
Cacodyl	4 vol. C + 12 vol. H + 2 vol. As = 2 vol. Kd	7·101	7·281
Cacodyl oxide ...	2 vol. Kd + 1 vol. O = 2 vol. Kd O	7·555	7·833
Sulphuret Cacodyl	2 vol. Kd + 1 vol. S = 2 vol. Kd S	7·810	8·39
Chloride Cacodyl .	1 vol. Kd + 1 vol. Cl = 2 vol. Kd Cl	4·56	4·86
Chloride Cacodyl .	3 vol. KdCl + 1 vol. Kd O = 4 vol. 3 KdCl + KdO	5·46	5·30
Cyanuret Cacodyl .	1 vol. Kd + 1 vol. Cy = 2 vol. Kd Cy	4·65	4·54.

This radical possesses the following properties:—

It is a clear, thin, highly refracting liquid, very similar to oxide of cacodyl; it has the same smell but is more inflammable. A glass rod moistened with it immediately takes fire when exposed to the air: its boiling point is about 170° C. At −6° C. it crystallizes in large square prisms; if the substance is pure it becomes like ice. It burns in oxygen gas with a pale blue flame, and forms water, carbonic and arsenic acids, which rise in the form of a white smoke. If the air is not in sufficient quantity for the combustion Erytrarsin is formed, and a black stinking mass of arsenic remains. In chlorine it burns with a clear flame and deposits carbon. Digested with hydrochloric acid and metallic tin it is converted with the appearance of various products into erytrarsin. The same substance is produced by the action of phosphorous acid, chloride of tin, and other powerful reducing agents. Fuming sulphuric acid dissolves the radical without combining with it. In the cold a quantity of sulphurous acid is evolved, and on distillation it gives off a substance with an agreeable æthereal odour, which appears to be sulphate of ætherol.

2. *Formation of the Compounds of Cacodyl from their Radical.*

The relative condensation of the gaseous compounds of cacodyl and the transformations which they undergo, give a great degree of probability to the theory of organic radicals, which is now rendered perfectly incontrovertible by the power of this radical to form directly the compounds from which it was separated. The whole series of compounds already considered can be formed either in the direct or in the indirect way, and the conditions under which this happens are precisely those observed with regard to the metals. The indirect action of oxygen, as well as the action of most of the oxidizing agents, occasions an increase of temperature in the formation of both the oxide and the acid of this radical; and from the first, by the action of hydracids, we obtain the corresponding combinations with sulphur, selenium, tellurium, chlorine, iodine, bromine, and cyanogen. By the treatment of the so-formed chloride with chloride of copper, chloride of platinum, chloride of palladium, &c., certain dou-

ble chlorides are formed, which I intend to refer to hereafter. When the radical is dissolved in nitric acid, and nitrate of silver is added, a very considerable precipitate is produced in the form of regular octahedral crystals, consisting of a combination of the latter salt with oxide of cacodyl, which appears to act the same part as constitutional water in salts. A solution of corrosive sublimate occasions the immediate formation of an oxychloride in the form of fine silky crystals, composed of 1 atom of oxide of cacodyl combined with 2 atoms of chloride of mercury.

Oxidizing agents are not the only bodies which act in a direct manner; other combinations are also formed in the same way. Sulphur in small quantities is acted upon by the radical, being dissolved by it, and forms a clear solution possessing all the properties of sulphuret of cacodyl, producing with solutions of oxides of lead and silver, sulphurets of these metals, and sulphuretted hydrogen with acids. Upon the addition of a large quantity of sulphur a higher sulphuret is formed, which is solid, and soluble in æther; from which latter solution it may be obtained in fine crystals. When to cacodyl a solution of chlorine is added, its yellow colour is immediately destroyed, together with its bleaching power; chloride of cacodyl is formed, which, acted upon by acids, gives hydrochloric acid. All these reactions, to which many more might be added of a not less striking nature, prove that this radical acts the part in every instance of a simple electro-positive element, *and that it is in fact a true organic metal.*

3. *Decomposition of the Radical.*

When the radical is distilled with anhydrous chloride of zinc it is decomposed, and forms several compounds at different temperatures. In order to ascertain more precisely the nature of this decomposition, pure chloride of cacodyl was digested with zinc in a distillation tube, until the whole solution was converted into a white mass of salt; the heat was then increased by means of an oil-bath to 200° C.; a perfectly clear fluid distilled over. When at this temperature nothing further passed over, the heat was increased to 220° C. and then to 260° C. It appeared to me dangerous to attempt any further decomposition by increasing the temperature; the attempt was therefore given up at this point.

After the apparatus was cool and the receiver taken off, there was no perceptible smell of any gaseous product. The substance which distilled over was again sucked up into a fresh distillation tube containing zinc, and by means of a continued digestion the last traces of chlorine were separated. The di-

stillation was effected by means of an oil-bath. When at the temperature of 100° C. nothing more came over, the receiver was separated; its contents (No. 1.) were removed into a tube filled with carbonic acid, with all the precautions already mentioned, and again sucked up into a fresh distillation tube, and re-distilled at from 100° to 170° C. The product (No. 2.) was put up also into tubes. The residue which remained in the distillation tube at 170° C. was again, for the third time, removed into a fresh distillation apparatus, and again distilled at from 170° and 200° C. without leaving behind any perceptible residue, and forms No. 3. All the three distilled products were quite transparent, æther-like, very liquid, and quite free from chlorine. The first scarcely took fire of itself, had a strong æthereal smell, and remained liquid at −18° C. The two others were exceedingly inflammable, and crystallized at − 8° C. in large prismatic crystals like cacodyl.

Tested with corrosive sublimate, the first gave but little appearance of containing cacodyl; on the contrary, the two last appeared to contain a considerable quantity. Analysis gave—

No. 1. First Distillation.

Substance	0·561
Carbonic acid	0·5875
Water	0·3665
Tube before burning	80·261
... after burning	79·310.

No. 2. Second Distillation.

Substance	0·5403
Carbonic acid	0·5140
Water	0·3145
Tube before burning	74·976
... after burning	74·147.

No. 3. Third Distillation.

Substance	0·5930
Carbonic acid	0·4265
Water	0·2635
Tube before burning	83·0195
... after burning	82·3270.

These results (a repetition of which, I think, unnecessary, as the weighing of the tube after burning serves as a check upon them) give the following compositions:—

	1st distillation, at 90° to 100° C.		2nd distillation, at 100° to 170° C.		3rd distillation, at 170° to 200° C.	
	equiv.		equiv.		equiv.	
Carbon . . .	4	28·95	4	26·31	4	19·88
Hydrogen .	6·1	7·26	6·05	6·46	6·1	4·82
Arsenic . . .	1·3	64·31	1·7	67·15	2·55	75·50
		100·52		99·92		100·23.

It follows from the analysis, that this radical, on distillation with chloride of zinc, undergoes a catalytic decomposition without the separation of arsenic, dividing into two or more compounds, in which the same quantity of carbon is combined with different quantities of arsenic; a circumstance of much interest as regards the theory of organic radicals. It is therefore probable that cacodyl, like arsenic, is a binary radical composed of $C_4 H_6$, and that its constituent elements are combined in such a manner that the compound of the cacodyl series are repeated in a similar way, only of a higher order. The above-described products of decomposition undergo, at a temperature of about 400° to 500° C., a decomposition, which I am in hopes, from the peculiarities in the constitution of the radical, to direct attention to. When cacodyl, or the before-mentioned mixure of the product of decomposition, is heated in a bent retort over mercury, the gas of this substance is decomposed, at a temperature little exceeding the boiling point of mercury, into metallic arsenic and a mixture of a compound of carbon and hydrogen, without the separation of a particle of carbon.

This gaseous substance burns with a variegated light flame, with a very slight deposition on glass of metallic arsenic. A solution of sulphate of copper, or nitrate of mercury, has no action upon the gas, however long it may remain in contact. With chlorine over water it takes fire, like a mixture of phosphuretted hydrogen, and burns with deposition of carbon, producing a red-coloured flame. Mixed with oxygen gas and inflamed by the electrical spark, it explodes more powerfully than fulminating gas, and generally breaks the vessel. Eudiometrical examination of the gas gives the following results:—

	1.	2.	Calculated.
Volume of the gas	1·4	1·5	1·5
Oxygen gas consumed . .	3·5	3·4	3·5
Carbonic acid formed . . .	2·0	2·0	2·0

These trials exactly agree with a compound in which the combination with the carburetted hydrogen in the cacodyl gives

4 volumes of vapour of carbon,
12 volumes of hydrogen,

condensed into 6 volumes.

I was at first induced to suppose that a similar decomposi-

tion of cacodyl took place as in the case of cyanide of mercury, as the action of this gas with chlorine did not agree with the action of any of the compounds from which this mixture of gases could in any manner arise; but the uncommon condensation, the essential circumstance in this case, appeared little to support this view. I have therefore continued the examination, and found that the burning with chlorine arises from the presence of a small quantity of a volatilizable compound of arsenic, which does not separate from the mixture, and which is at the same time the cause of the small stain of arsenic, which, on burning this gas in oxygen, remains on the side of the eudiometer. The true nature of this gas, given out by heat from cacodyl, is shown by the action of fuming sulphuric acid. This absorbs nearly one-third, and leaves behind an inodorous gas, burning pale blue, which is not altered by chlorine in the dark: in the direct rays of the sun, however, as Melsens has shown of the gas of the acetates and of marshes, it is condensed into oily camphor-like odorous bodies, in the state of small white radiating crystals. From a eudiometrical analysis of this gas, it appeared to be pure marsh gas. I found

From the volume examined . . .	19·2
Oxygen consumed	41·1
Carbonic acid formed	21·8

There can, therefore, be no doubt that the carburetted hydrogen, $C_4 H_6$, formed on the decomposition of cacodyl at a high temperature, is not separated as such, but that there are formed under these circumstances, two volumes of marsh gas and one volume of olefiant gas, viz.

$$C_4 H_6 As_2 = \begin{cases} C_2 H_4 \\ C_2 H_2 \\ As_2 \end{cases}$$

The examination of the gas not absorbed by the sulphuric acid confirms this view of the question; as one volume and a half of the pure gaseous mixture, which contains one volume of olefiant gas, and two volumes ($C H_2$) of marsh gas, must, in fact, upon burning with three and a half volumes of oxygen, produce two volumes of carbonic acid.

Whilst the absence of arsenietted hydrogen and free hydrogen decidedly proves that the first is not to be considered as a constituent element of cacodyl; the conclusion may be drawn, at the same time, from these appearances of decomposition, that if the radical $C_4 H_6$ can exist independently, it is most unstable and is decomposed much below a red heat.

Among the products of the decomposition of cacodyl, there is one substance which I have mentioned several times, and to which I have given the arbitrary name of *erytrarsin*. I shall now consider this substance, as it is in close connexion with the foregoing substances. I have not hitherto succeeded in obtaining any quantity of this remarkable substance. It is formed as a secondary product in the formation of chloride of cacodyl, sometimes in a great and sometimes in a small quantity. It is also deposited upon the distillation of oxide of cacodyl with water. Upon conducting the vapour of cacodyl, or oxide of cacodyl, through tubes slightly heated, this substance is produced in large quantities by an imperfect combustion; but, obtained in this manner, it is always contaminated with arsenic, from which it is impossible to separate it. The substance next made use of in preparing it was obtained in the following manner.

About 100 grammes of oxide of cacodyl was added to concentrated hydrochloric acid; chloride of cacodyl was formed, and a red flocculent precipitate fell, which, after distillation of the chloride, remains behind in the retort. The precipitate became during the distillation of a thick consistence, which increased, and became of a darker colour, with the appearance of finely divided red oxide of iron. After six or eight boilings with absolute alcohol, the substance was obtained quite pure and free from chlorine. It is necessary during this boiling to protect it from the air and to dry the substance in a vacuum with sulphuric acid, as otherwise it is liable to absorb oxygen slowly. Prepared in this manner, erytrarsin is of a steel blue shading into dark red, free from smell, and without the least appearance of crystallization. It is easily rubbed down into a red powder, which absorbs oxygen slowly from the air, with the appearance of the formation of arsenious acid, as it becomes covered with a white powder. This decomposition does not take place until after exposure for several weeks. It is not soluble in alcohol, æther or water—even caustic potash does not act upon it. In concentrated and not fuming nitric acid, it is soluble with decomposition. Red fuming acid occasions oxidation with inflammation. Heated in the air, it burns with an ash-coloured arsenical flame, without leaving any residue. Heated in a glass tube, it gives out vapours smelling of cacodyl, and deposits carbon, arsenious acid, and a ring of arsenic. The quantity produced from 100 grammes of oxide amounted to a little above 0·5 gramme. From the want of a sufficient quantity of this substance, I have only been able to make one analysis, which I however trust is sufficient, as every precaution was taken to ensure its accuracy.

0·394 gr. of the dried substance was burned with oxide of copper, and gave 0·1223 carbonic acid, and 0·074 water.

The arsenic was ascertained from the contents of the burning tube. These were dissolved in nitric acid, the solution diluted with water, and partly precipitated by carbonate of soda. The solution filtered from the copper was perfectly free from arsenic. The precipitate dissolved in hydrochloric acid, to which sulphuret of soda was added, also produced no precipitate of arsenic. The filtered solution gave, after being boiled with sulphurous acid in the usual manner, 0·7191 sulphuret of arsenic; of which 0·6333, acted upon by nitric acid, gave 0·0528 sulphur, and 2·1566 of sulphate of barytes. The following are the results:—

		Calculated.	Found.
C_4 . . .	305·76	8·73	8·58
H_6 . .	74·88	2·14	2·08
As_6 . .	2820·24	80·56	81·56
O_3 . . .	300·00	8·57	7·78
	3500·88	100·00	100·00

The difference of one per cent. in the arsenic found is accounted for from a small quantity of sulphuret of copper which was contained in the sulphuret of arsenic, which, on account of its small amount, could not be ascertained. The atomic weight of this substance I have not been able to ascertain in a direct way, as it does not enter into any direct combination; but the probability is, from the relation it holds to cacodyl, and to oxide of cacodyl, that that stated above is correct. I have therefore shown that the radical of the cacodyl series is converted, at a temperature approaching to redness, into marsh gas and oil gas, which gases may be considered as decomposing products of a non-isolated carburetted hydrogen, $C_4 H_6$. From what precedes it also follows, that of three atoms of oxide of cacodyl two atoms are decomposed in the manner described, while one atom of erytrarsin is left behind:—

3 atoms of oxide of Cacodyl, $C_{12} H_{18} As_6 O_3$
2 atoms of $C_4 H_6$ . . . . . $C_8 H_{12}$ $= 4 C H_2 + 4 C H$
$C_4 H_6 As_6 O_3$

The rational constitution of this compound can only be conjectured. As cacodyl in combination with oxygen undergoes the same decomposition at a higher temperature as in an uncombined state, it follows that erytrarsin may be considered as the oxide of a ternary radical, which can be distinguished from cacodyl only by its containing three times as much

arsenic. The complete examination of such a substance would be attended with great danger and many difficulties.

IX. *On the employment of Chromic Acid as an Agent in Voltaic Arrangements.* *By* R. Warington, *Esq.*

Read December 7, 1841.

In a paper "On the Action of Chromic Acid upon Silver," published in the Philosophical Magazine for December 1837, which action was effected by means of a mixture of bichromate of potash in solution and sulphuric acid, I concluded by stating, that in a future communication I hoped to consider the action of the same agents on other metallic bodies. The investigation has been resumed when my engagements permitted, and a great variety of interesting facts on this subject collected; but many analyses will still be necessary to render the subject complete, before the whole results can be submitted to the scientific world.

On making some new experiments, some time since, with the mixture of bichromate of potash and sulphuric acid referred to, I was led to believe that it would form a valuable and powerful agent in voltaic arrangements from possessing the following advantages over every other liquid hitherto employed for the same purpose, namely, the high degree of energy with which it acts upon certain metals, the facility with which it is decomposed by deoxidizing agents, as hydrogen gas and numerous others, with the circumstance that in all these actions of oxidation no gaseous matter is evolved.

My first endeavour was to substitute this mixed fluid for the nitric acid in the powerful arrangement of Professor Grove, so as, if possible, to obviate the inconveniences arising during the action of that battery, without diminishing the splendid effects produced by it. In doing this it was absolutely necessary, from the nature of the materials to be employed, to modify to a certain extent the details of the construction of the battery, retaining the metallic elements unaltered, but enlarging considerably the cell appropriated for the nitric acid. Now as the dilute sulphuric acid in the zinc cell of the battery remains the same in both cases, it will be only necessary to show, by the constitution of the nitric acid and the bichromate of potash, the relative value of these two oxidizing agents in terms of the quantities of the available oxygen they contain, such oxygen combining with the hydrogen eli-

cited by the action of the dilute sulphuric acid on the zinc element.

Liquid nitric acid, of 1·48 sp. gr., is composed of 74 parts by weight of real acid and 26 of water, and these 74 parts contain 32·9 of oxygen and 41·1 of binoxide of nitrogen, which latter body is given off in a gaseous state, as soon as the undecomposed nitric acid has become saturated with it, and assumed a deep green tint. When liberated from the solution the gas combines with the oxygen of the air, generating the nitrous and hyponitric acids, the red noxious vapours which render the use of this form of battery so inconvenient. There must, I imagine, be also a considerable loss of power from this evolution of gaseous matter. I am not aware to what extent the decomposition of the nitric acid can be carried in Grove's battery, for after the action has been going on about five hours, an effect of endosmosis commences between the cells through the pores of the biscuit earthenware, and the amalgamated zinc plates are attacked with rapidity and quickly destroyed. Not expecting such an occurrence, I had left a small battery in action, on one occasion, through the night, and found in the morning, to my great annoyance, that the whole of the zincs were destroyed, and the arrangement all fixed together.

Bichromate of potash is composed of 2 equivalents of chromic acid, or 104 parts by weight, and 47·5 of potash, and these 104 parts contain 80 of the green oxide of chromium and 24 of oxygen. Consequently, to obtain the same quantity of available oxygen as we have in the 100 parts of nitric acid, supposing the decomposition of these to be complete, we shall require 206·9 of bichromate; and to convert this into the double sulphate of chromium and potash, or chrome alum, 275·8 of concentrated sulphuric acid will be necessary. These proportions of materials are requisite, as it is the strong affinities leading to the formation of chrome alum which give rise to the energetic oxidizing action of this mixture.

A number of experiments were tried, to ascertain whether the action of a battery excited by the acid element described would be sustained and continuous, and the results have fully established that it is so. In the action of such a battery no gaseous matter is given off, the oxygen of the chromic acid combining with the hydrogen from the zinc cell to form water, as is the case where nitric acid is employed. And as the deoxidized chromic acid, or the oxide of chromium formed, combines with the sulphuric acid and potash immediately as it is produced, no injurious effect can arise from diffusion between the cells; the whole process goes on steadily and without in-

termission, until either the sulphuric acid in the zinc cell is saturated with the oxide of zinc, or the whole of the chromic acid of the bichromate is deoxidized.

Various other arrangements, in which bichromate of potash is used mixed with sulphuric, muriatic, nitric, and acetic acids, with the usual, and also with different, metallic elements, are under investigation; and the results obtained, with their comparison with other batteries, will be laid before the Society at an early period.

X. *On a new Class of Cacodyl Compounds containing Platinum.* By *Professor* Bunsen *of Marburg**.

Read December 7, 1841.

IN a former paper I have endeavoured to prove, from the numerous instances of substitution presented by *alcarsin*, that this substance contains a ternary radical, composed of *arsenic* united to a *carbo-hydrogen* ($C_4 H_6 + As_2$), and entering into composition with elementary bodies like a metal, in a manner not hitherto observed. This opinion has been confirmed by my subsequent experiments, and may be considered of considerable importance in the question of compound radicals. The *chloride* of this radical is reduced by those metals which decompose water, at a temperature not exceeding that of boiling water; the free radical separating in the form of a clear æthereal fluid, which oxidates in the air with more rapidity than potassium, and produces two degrees of oxidation by its combustion, namely, an acid and an oxide, both of which can be again reduced by deoxidizing agents. The analogy between cacodyl and the metals extends still further; for that radical unites directly with the non-metallic elements, forming substances of the same nature as are produced when hydracids combine with the elements of metallic oxides, water being produced.

It will be seen, from what has been said, that this substance bears a greater resemblance than most other compound bodies to *ammonia*. Under this impression I tried the action of *chloride of platinum* on it, and have been fortunate in obtaining a class of compounds analogous in composition to those of Gros and Reiset; supposing the ammonia in the latter replaced by cacodyl. The results obtained tend to throw a new light on the relations in which the organic bases, or alkaloids, stand towards the simple oxides of metals.

* Translated from the German MS. of the author by Dr. T. G. Tilley.

Chloride of Cacoplatyl.

By mixing an alcoholic solution of chloride of platinum with a similar solution of chloride of cacodyl, a precipitate of a reddish-brown colour is obtained, which, when washed with alcohol and reduced to powder, becomes yellowish-red, and is inodorous. When this powder is heated, it melts into a clear yellow gummy mass, gives off hydrochloric acid and vapours smelling of chloride of cacodyl, and leaves behind a gray-coloured arseniuret of platinum. Both the chlorides of platinum and cacodyl are indicated in this compound by reagents. Should this compound be analogous to the chloride of cacodyl, its composition would be, Pt Cl + Kd Cl. This body, however, could not be analysed, for it is so easily decomposed as not to be of uniform composition. If the precipitate in question be boiled with water, a yellowish solution is formed, alcargen being generated at the same time, and the solution on cooling deposits white needle-shaped crystals. This substance may be named *chloride of cacoplatyl*, and from this name the others will be derived. To obtain the chloride of cacoplatyl in larger quantities and in a more easy manner, an aqueous solution of chloride of platinum is boiled with chloride of cacodyl. The precipitate, which falls first of a brown colour, is changed by boiling into a wine-yellow colour. The precipitation of the chloride of cacoplatyl commences even during the boiling, and by cooling still more is deposited. The mother liquid contains nothing except a little alcargen (or perhaps a true salt of cacodylic acid and oxide of platinum). The crystals are collected on a filter, and purified by redissolving. This compound possesses the following properties:—it crystallizes from a hot solution in long sharp needles, which are beautifully formed, is inodorous, its taste disgustingly arsenious. It is soluble in hot alcohol and water, more sparingly so in these liquids cold. When heated it becomes yellow, then brown, and without melting takes fire and burns like tinder, giving off vapours smelling of arsenic, and leaving behind fusible arseniuret of platinum. Sulphuric acid, by depriving the compound of water, turns it yellow. Hydrochloric acid has no action. In ammonia it is soluble in all proportions; by evaporating the solution, imperfect crystals are formed, which are insoluble in alcohol. Iodide of potassium produces in the solutions of chloride of cacoplatyl a yellow precipitate, which dissolves of a reddish-brown colour in ammonia. With bromide of potassium, a compound crystallizing in long silky needles is formed. Cyanide of potassium gives a yellowish white precipitate. By nitrate of silver,

the chloride of silver is thrown down, without destroying the neutrality of the solution.

The elementary analysis of the chloride of cacoplatyl, dried at 110° C., was made by means of oxide of copper in a combustion tube, the free space left in the tube being filled with turnings of copper*. In a second analysis, chromate of lead was used; the results were the same:—

	1.	2.
Substance	1·440	1·0194
Carbonic acid . .	0·494	0·3480
Water.	0·356	0·2475

The chlorine was estimated by heating the compound to redness with caustic lime. 1·0873 gramme of substance gave 0·580 chloride of silver, or 0·0225 silver; by direct precipitation from the solution by nitrate of silver, from 0·987 of substance only 0·353 chloride of silver, or 0·1405 silver was obtained. The estimation of the platinum and arsenic is attended with some difficulty, from the circumstance that chloride of cacoplatyl is not perfectly oxidized by nitric acid. 0·850 gramme was therefore heated in a combustion tube, with a mixture of 1 part of carbonate of soda and 3 parts of chlorate of potash. The contents of the tube, after digestion with water, left a quantity of arseniuret of platinum. The solution, which was coloured yellow by a little of the double chloride of platinum and potassium, was thrown on a filter, and the arsenic containing platinum again collected. This last was dissolved in aqua regia, and some silicic acid derived from the combustion tube separated. The fluid, freed from silicic acid, and evaporated to dryness, was again dissolved in weak alcohol, and gave 0·752 gramme chloride of platinum and potassium. Besides this, 0·018 platinum was obtained by heating a quantity of sulphuret, formed by transmitting through the solution a stream of sulphuretted hydrogen. The fluid, when filtered, was made use of for obtaining the quantity of arsenic; it was freed from alcohol by boiling, deoxidized by sulphurous acid, and precipitated by sulphuretted hydrogen. It gave 0·458 of sulphuret of arsenic, from which, by oxidation with nitric acid, 1·254 of sulphate of barytes was obtained.

These analyses conduct to the following formula for chloride of cacoplatyl:—

* This precaution is necessary, lest some chloride of copper be carried into the chloride of calcium tube with the watery vapour; when metallic copper is present, a basic chloride of copper is formed, which is not volatile.

			1.	2.	
Carbon	C_4 . .	305·7	9·44	9·49	9·52
Hydrogen	H_7 . .	87·4	2·70	2·75	2·73
Arsenic	As_2 .	940·0		29·54	29·29
Platinum	Pt . .	1233·3		37·98	38·34
Chlorine	Cl . .	442·6	13·48	13·85	13·79
Oxygen	O_2 . .	200·0		6·39	6·32
		3209·0		100·00	100·00

The agreement between the carbon, hydrogen, and chlorine found, and the numbers obtained by calculation, proves without doubt that the following empirical formula, $C_4 H_7 As_2 Pt Cl O_2$, is correct. It appears certain that this compound contains an atom of water, not as water of crystallization, but in another form, for the compound may be heated to 164° C. without decomposition. At that temperature the colour is changed to a citron yellow, and an atom of water is given off, which however is reacquired when the substance is boiled with water. 0·9767 loses, by 210° C., 0·037, and no more, although the temperature is raised to 240° C. The compound contains therefore 3·79 per cent. of water, which corresponds to 1 atom, and can be replaced by 1 atom of ammonia.

Bromide of Cacoplatyl.

This compound is formed when a hot solution of the chloride of cacoplatyl is mixed with bromide of potassium; the crystals obtained are redissolved and recrystallized twice. They possess great similarity to the chlorine combination, and form small yellow needles by the quick cooling of the aqueous solution; but when the solution is allowed to cool gradually, the crystals formed are large, well-shaped, and colourless. They are pretty soluble in hot, but only sparingly soluble in cold water. They have a feeble acid reaction, are inodorous, but possess a decidedly disagreeable arsenical taste, which is bitter and astringent, and remains long on the palate, suggesting alcarsin. At 120° C. they lose their water and become yellow. At 240° C. this compound begins to be decomposed, becoming gray at that temperature; and when the heat is increased to 246° C. it melts into a black fœtid mass. At a higher temperature it takes fire in the air, and burns like tinder, leaving the arseniuret of platinum in shining scales. The analysis of this compound is equally simple with that of the preceding chlorine compound, and is made by combustion with oxide of copper; the anterior part of the tube being filled with copper turnings.

Dried at 100° C.	1.	2.
Substance	0·8835	1·1347
Carbonic acid . .	0·268	0·3473
Water	0·190	0·0249

To estimate the quantity of the bromine, 0·7145 gramme was dissolved in water, precipitated by nitrate of silver, and boiled some time with nitric acid, by which 0·452 bromide of silver was obtained. This research gives the following numbers:—

			Calculated.	1.	2.
Carbon	C_4 . .	305·76	8·17	8·16	8·37
Hydrogen	H_7 . .	87·36	2·33	2·39	2·41
Arsenic	As_2 .	940·08	25·10		
Platinum	Pt . .	1233·26	32·93		
Bromine	Br . .	978·30	26·13	26·56	
Oxygen	O_2 . .	200·00	52·34		
		3744·76	100·00		

To determine the proportion of water in the substance, 1·2534 gramme was dried at 100° C. and then heated in an oil-bath at 200°, till no more weight was lost. The loss was 0·040, which is equal to 3·200 per cent. It will be seen that this compound, like that of chlorine, contains 1 atom of water.

The formula for the hydrous and anhydrous compounds respectively are

$$Pt\,O_2\,C_4\,H_7\,As_2\,Br,$$
$$Pt\,O\,C_4\,H_6\,As_2\,Br.$$

In this compound also the water can be replaced by ammonia.

Iodide of Cacoplatyl.

The yellow precipitate which iodide of potassium forms with chloride of cacoplatyl is this iodide. By mixing the two solutions, boiling hot and tolerably dilute, the iodide separates in the form of glistening scales of a silky lustre, resembling the iodide of lead. It possesses nearly the same degree of solubility in water as the last-named substance.

The iodide differs from the other compounds of cacoplatyl in losing its whole water at 100° C.; it becomes then of a brown violet colour without melting. The brown crystals dissolve in water, forming a yellow solution, which deposits crystals again on cooling.

This compound also is inodorous, and may be submitted to a high temperature without decomposition. It is injured at 260° C., when the compound melts and becomes black, giving off dark vapours smelling like alcarsin, and, lastly, burns like tinder, leaving the arseniuret of platinum. For the analysis of this substance, it was dried and burned with oxide

of copper and copper-turnings, which last prevent any error arising from iodine passing over.

	1.	2.
Substance. . .	1·4322	1·146
Carbonic acid	0·3745	0·300
Water	0·2510	0·400.

To estimate the iodine, 0·6685 of the salt, dried at 100° C., was precipitated from solution by nitrate of silver, the precipitate being afterwards boiled in nitric acid. This trial gave

			Calculated.	1.	2.
Carbon	C_4 . .	305·76	7.22	7·23	7·24
Hydrogen	H_6 . .	74·88	1·77	1·95	94
Arsenic	As_2 .	940·08	22·22		
Platinum	Pt. .	1233·26	29·14		
Iodine	I . .	1578·28	37·29	36·58	
Oxygen	O . .	100·00	2·36		
		4232·62	100·00		

Sulphate of the Oxide of Cacoplatyl.

To prepare this compound, a solution of 20 parts of the chloride of cacoplatyl, dried at 100° C., is boiled with 12·17 parts of dried sulphate of silver till the solution is not rendered turbid by salts of silver or chlorine. The filtered fluid is evaporated *in vacuo* over sulphuric acid till crystallization begins. At this degree of concentration a trace of the chloride of silver, which had remained dissolved, is precipitated. The chloride of silver is separated by filtration, and the solution again evaporated *in vacuo* and over sulphuric acid, till the greater part of the salt is deposited. The salt is purified by pressing it between folds of bibulous paper. Thus prepared it has the form of white hard crystalline grains, which appear, under the microscope, to be prismatic. This salt is inodorous, but possesses a bitter and astringent taste, which after a time suggests a relation to the cacodyl compounds. It does not deliquesce, nor is it decomposed by contact with air. It may be heated to 160° C. without injury; a few degrees higher its colour becomes gray, then black, giving off vapours smelling of cacodyl, and, lastly, it takes fire and burns like amadou, leaving behind an arsenical compound containing platinum, which is fusible.

To ascertain the quantity of water contained in this compound, 1·078 gramme was dried for 24 hours over sulphuric acid, and then again for six hours at a temperature of 100° C.: the loss of weight was 0·0045 gramme. By heating it for three hours longer at 140° C. it lost 0·0025 gramme. It thus appears that this compound parts with its hygroscopic water

with difficulty. It contains no more water which can be driven off by any elevation of temperature. 1·0390 gramme of this salt, dried at 140° C., burnt with chromate of lead, gave 0·2395 water, and 0·340 carbonic acid.

0·5491 gave 0·1290 water, and 0·175 carbonic acid.

1·0474 gramme dissolved and precipitated by nitrate of barytes, gave 0·04746 sulphate of barytes.

These determinations give the following composition:—

			Calculated.	1.	2.
Carbon	C_4	305·7	9·08	8·81	8·81
Hydrogen	H_7	87·4	2·60	2·56	2·61
Arsenic	As_2	940·0	27·91		
Platinum	Pt	1233·3	36·62		
Oxygen	O_3	300·0	8·91		
Sulphuric acid	SO_3	501·2	14·88	15·57	

The characters of the chloride of cacoplatyl are so well marked, and its relations to other bodies so manifest, that we cannot be in doubt for a moment as to its rational composition. One glance at its empirical formula will satisfy us that here, as in the compounds of cacodyl, the most electro-negative element, chlorine, can by analogy be replaced by bromine and iodine, just as oxygen is replaced by sulphur. The manner in which this substitution takes place is not different from that which we observe in the inorganic saline compounds. The chloride of cacoplatyl, treated with the iodide of potassium, gives up its chlorine to the potassium, while the iodine goes over to the other element of the formula, from which the potassium has withdrawn the chlorine. The order of affinity of chlorine, iodine, and bromine, for the substance in question, bears a perfect analogy to what we observe in the inorganic haloid salts. The iodine is here set free by chlorine and bromine, as in these salts, while bromine is removed by chlorine only.

Such an agreement in relation shows a similarity in the form of the groups of the elements, and indicates that here, as in the inorganic haloid compounds, there are two divisions in the formula, one of which represents the metal, the other the halogenous body or salt-radical. We can express it thus:—

$$Pt\,O_2\,C_4\,H_7\,As_2 + Cl.$$

The first division of this formula, which I have called cacoplatyl, represents a peculiar and remarkable radical, forming classes of compounds possessing great interest, and giving an insight into the relation in which the vegeto-alkalies stand with regard to organic radicals. As the vegeto-alkalies, when heated, give off ammonia, so our compound gives off water, and this water can be replaced by oxides of metals. If we

remove this atom of water in the formula, we have remaining one atom of oxide of platinum, and one atom of cacodyl, which will explain the formation of these compounds in the simplest manner. The rational expressions may be thus given :—

For the anhydrous chlorine compound . . . . . $PtOKa + Cl$
For the hydrous . . . . . $HO\ PtOKa + Cl$
For that containing ammonia . . . . . $NH_3\ PtOKa + Cl$
For the oxide . . . . . $HO\ PtOKa + O$
For the sulphate . . . . . $(HO\,PtOKa + O)\,SO_3$

The nature of this composition proves that the power of inorganic *acids* to unite with certain organic bodies, without losing their power of saturation, is not alone possessed by acids, but that *bases* have also the same property; for in the present case, the oxide of platinum bears a relation to the oxide of cacodyl similar to that which sulphuric acid does to benzoic acid in sulpho-benzoic acid. In the latter, the benzoic acid is as little indicated by reagents as the oxide of platinum in the cacoplatyl; and as the double acid referred to neutralizes only one atom of base, so the double base in question saturates only one atom of acid, or that quantity which the quantity of oxygen in the oxide of platinum indicates.

A comparison of this new class of compounds with that discovered by Gros and Reiset, will afford another reason for admitting the constitution which has been assigned to them. Reiset has rendered certain the existence of a body, composed of the elements of 1 atom water, 2 atoms ammonia, and 1 atom oxide of platinum, which does not lose its atom of water when it enters into combination with oxygen acids, and contains, precisely as cacoplatyl, 2 atoms of oxygen, and saturates 1 atom of acid. Berzelius affirms that these salts contain the oxide of ammonium. Here ammonia is combined with the oxide of platinum, as the naphthaline is in sulpho-naphthalic acid, viz. $(PtONH_3, NH_4 + O)\,SO_3$.

The simple relation in which this salt stands to the cacoplatyl compound must therefore not be passed over. The latter is nothing else than such a salt, in which the ammonium is replaced by cacodyl. Its relation to ammonium in the electrical series of compound radicals is like that of an electro-negative metal to an electro-positive one, as, for instance, iron to potassium. It cannot, however, be denied that, while the compound of Reiset is a strong caustic base, the oxide of cacoplatyl forms only salts of an acid reaction. The analogy which the vegeto-alkalies and their composition show is so great, that it permits no doubt as to the identity of their

constitution with that of this body. It now only remains for me to show, by comparison, the greatness of this analogy by the substitution of the platinum compound by an organic oxide.

Reiset's Compounds.	Comps. of Cacoplatyl.	Compounds of Quinine.
$N H_3, Pt O, N H_4 + Cl$	$\dot{H}\,\dot{Pt}\,Kd + Cl$	$(C_{20} H_8) O_2 N H_4 + Cl$
$N H_3, Pt O, N H_4 + I$	$\dot{H}\,\dot{Pt}\,Kd + I$	$(C_{20} H_8) O_2 N H_4 + I$
$N H_3, Pt O, N H_4 + O$	$\dot{H}\,\dot{Pt}\,Kd + O$	$(C_{20} H_8) O_2 N H_4 + O$
$(N H_3, Pt O, N H_4 + O) S O_3.$	$(\dot{H}\,\dot{Pt}\,Kd + O) S O_3.$	$(C_{20} H_8 O_2 N H_4 + O) S O_3.$

The formation of *urea* (a body which possesses all the properties of an organic base, and may be considered as a cyanate of oxide of ammonium) belongs to the same class of phænomena. In that compound an oxide of cyanogen (cyanic acid) occupies the place of the oxide of platinum in Reiset's ammonium compound, and unites with ammonium to give rise to a compound radical, if such it may be considered. The radical (Cy O, $N H_4$) which forms part of urea, is in every relation similar to cacoplatyl; the oxide of that radical, or urea, being of all this class of compounds that which approaches most closely to the oxide of cacoplatyl, (Cy O, $N H_4$) + O = urea.

XI. *On some of the Substances contained in the Lichens employed for the preparations of Archil and Cudbear.* By Edward Schunck, *Esq.*, *Manchester.*

Read January 4, 1842.

OUR knowledge concerning that department of organic chemistry which embraces the colouring matters, and other principles nearly allied to them, is of the most imperfect kind. Though many other branches of organic chemistry have been so thoroughly and accurately investigated, that little or nothing remains to be known concerning them, this may be called an unexplored field. Most of the colouring matters are so little known, as regards even their most essential characters, as not to allow us either to justify or to question the propriety of throwing them together into one general class; a class distinguished from those nearly allied to it merely by the (as far as we know) adventitious circumstance of the substances belonging to it being endowed with certain more or less vivid colours. Among all the colouring matters there are none, the study of whose properties and reactions is calculated to throw more light on the nature of the whole class, than those which are prepared by an artificial process from certain kinds of lichens, and on this account

it is desirable that they should be carefully examined. It was the circumstance of these substances being prepared artificially from plants perfectly devoid of colour that first attracted to them the attention of chemists, and led to a series of investigations by which a number of highly interesting substances was brought to light, and a process elucidated which belongs to the most remarkable and unparalleled in the whole range of organic chemistry.

Robiquet first discovered a colourless crystallizable substance in them (orcin), capable of being converted by the joint action of ammonia and oxygen into a true colouring matter, which contains neither the original substance nor ammonia as such. This interesting discovery was followed by others. The researches of Heeren made us acquainted with a series of substances contained in the *Roccella tinctoria*, possessed of the same property, and another substance, phloridzin, was shown by Stas to bear a complete analogy to orcin in this respect. The subsequent labours of Dumas, who subjected orcin and the bodies derived from it to an accurate examination, and of Kane, who has determined the composition of the substances discovered by Heeren, and of the colouring matters contained in archil and litmus, seemed to have sufficiently elucidated the subject. Some obscurities, however, in a part of Dr. Kane's late paper seemed to make it desirable that some of his results should be confirmed before being finally adopted, and at the suggestion of Professor Liebig I undertook the re-investigation of this subject, and performed it in his laboratory.

Instead of the *Roccella tinctoria* I employed in my experiments the lichens that grow on the basalt rocks of the Vogelsberg in Upper Hessia, where they are collected for the purpose of preparing a dye from them. These lichens were all crustaceous and belonged to the genera *Lecanora*, *Urceolaria*, *Variolaria*, &c. From them I extracted the following substances:—

1. A white crystalline substance, soluble in alcohol and æther but insoluble in water, bearing in its properties great resemblance to the substance called by Heeren *Erythrin* and by Kane *Erythrilin*, but different in composition, and giving other products of decomposition. This substance I call *Lecanorin*.

2. A crystallizable substance identical in properties and composition with Heeren's *Pseuderythrin* and Kane's *Erythrin*.

3. A fatty substance of acid properties, soluble in alcohol but insoluble in æther and water.

The method by which these substances were extracted and

separated from one another, was the following. The lichens were reduced to a coarse powder and then treated with æther, in an apparatus of displacement, until the æther dissolved nothing more. The æthereal extract, which had acquired a green tinge from chlorophyll in solution, was distilled off, leaving as a residue a greenish yellow mass, consisting for the greater part of lecanorin. This mass was brought into a glass funnel and washed with small quantities of æther, until it had lost its green colour in part. It was then treated with boiling water in order to remove every trace of pseuderythrin, and, lastly, purified by dissolving it in a small quantity of boiling alcohol, which deposited on cooling a snow-white crystalline mass, consisting of lecanorin in a state of purity. The dark green æthereal fluid obtained by washing the impure lecanorin, contained besides lecanorin the greatest part of the pseuderythrin which had been extracted by the æther. The fluid was evaporated to dryness and the residual mass treated with boiling water, which deposited on cooling a mass of shining plates and needles of pseuderythrin, which was purified by re-crystallization. More of this substance was obtained by treating the lichens, which had been exhausted with æther, with boiling alcohol and filtering rapidly. The alcohol was distilled off and the residue treated with boiling water, which dissolved all the pseuderythrin and deposited it on cooling. The mass left undissolved was washed with æther, which dissolved all the chlorophyll and left behind the fatty substance mentioned above, which was purified by re-dissolving in alcohol.

I will now proceed to a more minute description of the properties of these several bodies.

Lecanorin.

This substance, when pure, is perfectly white. If prepared in the manner described above, it has the appearance of a white mass composed of acicular needles. When its solutions are slowly evaporated, it crystallizes in silky needles grouped together in star-shaped masses. It is insoluble in boiling water, but soluble easily in alcohol and æther. Its solutions redden litmus paper. It is soluble in alkaline liquors, from which it is precipitated unchanged by acids, provided the solutions be not boiled and be not left to stand too long. It is insoluble in all weak acids, with the exception of acetic acid. Strong nitric acid converts it ultimately into oxalic acid. It combines with metallic oxides by double decomposition. Heated on platinum foil it melts, emits a dense vapour, and burns off, leaving but little carbonaceous residue. When heated in a tube closed at one end, it melts, and, under violent

ebullition, gives off a dense vapour, which condenses in the upper part of the tube into a thick liquid, which after some time solidifies, forming a crystalline mass. The nature of this sublimate will be explained further on.

The action of the alkalies on this substance is of course the most interesting point connected with its history. A solution of lecanorin in ammonia when exposed to the air, acquires after some time a beautiful deep purple colour: from this solution acids precipitate a red colouring matter. A solution in potash, under the same circumstances, becomes of a deep red colour. Being desirous of ascertaining whether the lecanorin was immediately converted into the red colouring matter, or whether it passed first through any intermediate state, which was not improbable, I dissolved some of the substance in ammonia, excluding the solution from contact with the air. After a lapse of some hours, the solution, though perfectly colourless, was found no longer to contain any lecanorin; for acids, instead of producing a thick gelatinous or flocculent precipitate, as they do when applied immediately after solution has been effected, merely caused a brisk effervescence of carbonic acid, plainly showing that the substance had been completely decomposed without a colouring matter having been formed. The same effect was brought about instantaneously when the solution was boiled. In order to observe the process more clearly, I dissolved a quantity of lecanorin in baryta water in the cold. The solution, on being boiled or allowed to stand, deposited a great mass of pure carbonate of baryta. The liquid was filtered rapidly, and the excess of caustic baryta precipitated by a stream of carbonic acid: on slow evaporation it yielded large prismatic crystals of a substance which possessed characters in every respect identical with those of *orcin*. It had an extremely sweet taste, was capable of being volatilised without change and without leaving any residue, gave a deep blue colour when dissolved in ammonia and exposed to the air, struck a blood-red colour with nitric acid, and precipitated a solution of basic acetate of lead. Lecanorin thus is converted by the action of alkalies into orcin and carbonic acid, in the first instance, this decomposition always preceding the formation of colouring matters. The same decomposition is produced by the carbonated alkalies, by long boiling with water and by dry distillation, the heavy vapour mentioned above as being produced by heating lecanorin to decomposition, being vapour of orcin.

The composition of lecanorin is expressed by the formula $C_{18}\ H_8\ O_8$. The results of the combustions which I made of it admit of no other interpretation. All attempts to determine

its atomic weight by means of combining it with metallic oxides, failed. These compounds can only be prepared by double decomposition; but the facility with which lecanorin is decomposed when alkalies are added to its solutions, always renders the purity of the compounds formed liable to doubt. The compound with oxide of silver, formed by adding nitrate of silver to an alcoholic solution of lecanorin, and then precipitating by means of a few drops of ammonia, though it changed colour but slightly in drying, gave no consistent results. The compound with oxide of lead, formed by precipitating a solution of lecanorin with basic acetate of lead, was so basic and its formula so unusual, that I am led to suppose that one or two atoms of basic acetate of lead were precipitated together with it. By decomposing, however, a weighed quantity of lecanorin with caustic baryta, and determining the quantity of carbonate of baryta formed, I obtained very accurate results, confirming the formula $C_9 H_4 O_4$, or $C_{18} H_8 O_8$, for lecanorin. In regard to the composition of orcin, I have been induced to replace the generally received formula for its composition by a new one. Dumas's formula for anhydrous orcin is $C_{18} H_7 O_3$, and for crystallised orcin $C_{18} H_{12} O_8$, which evidently cannot be brought into accordance with the formula for lecanorin as given above. If, however, the formula $C_{16} H_6 O_2$ be taken for anhydrous orcin, and $C_{16} H_{11} O_7$ for crystallized orcin, then the decomposition which lecanorin undergoes with alkalies may be expressed as follows:—

1 atom of anhydrous orcin . .	$C_{16} H_6 O_2$
2 atoms of water	$H_2 O_2$
2 atoms of carbonic acid . . .	$C_2 \quad O_4$
1 atom of lecanorin	$C_{18} H_8 O_8$

Two atoms of water are furnished by the decomposition of the lecanorin itself, and three more by the fluid, to form from $C_{16} H_6 O_2$ one atom of crystallized orcin, $C_{16} H_{11} O_7$. The combustions which I have made of this substance agree perfectly with these formulas, but Dumas's analyses of the lead compound of orcin, which I have myself not yet examined, do not coincide with them, unless it be supposed that this compound contains acetate of lead, either in chemical combination or mechanically mixed.

In regard to the numerical results from which the above formulas have been deduced, I shall reserve them for a future occasion, when, having completed the investigation of the whole class of substances of which those here described are only a part, I shall be able to enter more minutely into details, and exhibit the facts and numbers brought to light in

their proper connexion and order. I have merely been desirous of showing, on the present occasion, that our knowledge of this series of bodies is far from being complete. I have shown above, that the action of alkalies on lecanorin is twofold; it consists, first, in abstracting from the substance carbonic acid, a process not requiring the co-operation of the oxygen of the atmosphere; secondly, in inducing in contact with the air the formation of colouring matters. The first action seems to have been overlooked in the case of all the bodies nearly allied to lecanorin. I have found the most complete analogy in the case of Heeren's pseuderythrin; and, if I am not mistaken in the interpretation of his statements, his erythrin also undergoes the same decomposition as lecanorin, for the former is converted into erythrin-bitter by the very same agencies by which lecanorin is converted into orcin, and in fact there is the same relation in regard to all general properties between erythrin and erythrin-bitter as between lecanorin and orcin. This circumstance is of some importance, for in order to arrive at a knowledge of the exact composition of such complex bodies as the colouring matters formed by the action of alkalies on these substances, and to understand perfectly the nature of the process by which they are produced, it is absolutely necessary to know the exact substance out of which each is in the last instance formed, the last link of the chain which precedes its formation.

Pseuderythrin.

For this substance it would be advisable to substitute another name, as in this case the substance by which it is accompanied is not erythrin but lecanorin. It is contained in very small quantities in the lichens that I examined. It is sparingly soluble in cold water, but easily soluble in boiling water, from which it crystallizes on cooling in shining plates and needles. If more of the substance is taken than the boiling water can dissolve, the part left undissolved melts and collects at the bottom of the fluid in oily drops, which, on the temperature falling a little below 212°, congeal and form crystalline masses. This is a characteristic property of pseuderythrin, and one distinctly mentioned by Heeren. It is easily soluble in alcohol and æther, and also in alkaline solutions. It gives compounds with metallic oxides by double decomposition. When dissolved in ammonia and exposed to the air, it gives, like lecanorin, a red colouring matter; but its conversion into the latter is much more slowly effected than that of lecanorin. When subjected to dry distillation it also gives a crystalline sublimate, accompanied by a copious dis-

engagement of gas. When its solution in an alkali is boiled or left to stand some time, it imparts carbonic acid to the alkali, the decomposition being accomplished, however, with much more difficulty than with lecanorin. The exact nature of the substance left in solution after this decomposition I was unable to determine, on account of the very small quantity of pseuderythrin which I had at my disposal.

The combustions which I made of this substance confirmed the formula established by Liebig at the time of Heeren's investigation, viz. $C_{20}\ H_{12}\ O_8$.

The *fatty substance* mentioned above I have examined but slightly. It is soluble in alcohol, but insoluble in æther and water. From an alcoholic solution it is deposited in small pearly-white scales; if the solution be spontaneously evaporated, it is obtained in small, hard, shining, transparent crystals. It is soluble in alkalies, forming soapy solutions, and is re-precipitated by acids. Its alkaline solutions do not become coloured when exposed to the air. It cannot be melted without being decomposed.

XII. *On a Re-arrangement of the Molecules of a Body after Solidification.* *By* Robert Warington, *Esq.*

Read January 4, 1842.

HAVING occasion lately to prepare some alloys of lead for the purpose of lecture illustration, I was much surprised at an alteration taking place in the arrangement of the particles of one of these alloys, as shown by the appearance of the surfaces of fracture after the metal had assumed the solid form. The alloy experimented on was that known as Newton's fusible metal, composed of 8 parts of bismuth, 5 of lead, and 3 of tin. On pouring this alloy in the melted state on a marble slab, and breaking it as soon as solid, and when it may be readily handled, the exposed surfaces were found to exhibit a bright, smooth, or conchoidal metallic appearance, of a tin-white lustre; and the act of disjunction at one part will, frequently, cause the whole to fly into a number of fragments analogous to the breaking a piece of unannealed glass.

The metal after this becomes so hot as to burn the fingers if taken up and when this evolution of heat has ceased the alloy will be found to have entirely altered its characters, having lost its extreme brittleness, requiring to be bent to and fro several times before it will break, and presenting on fracture a fine granular or crystalline surface of a dark colour and

dull earthy aspect. Similar phænomena accompany the casting of the fusible alloy of H. Rose, composed of 2 parts of bismuth, 1 of lead, and 1 of tin.

The fact of the evolution of heat from the alloy of Newton, and its cause, are thus noticed by Berzelius in his *Traité de Chimie*. "If this alloy is plunged into cold water and quickly withdrawn and taken in the hand, it becomes sufficiently hot after a few moments to burn the fingers. The cause of this phænomenon is, that during the solidification and crystallization of the *internal parts* the latent heat of these is set free and communicates itself to the surface before the fixing and cooling." The alteration in the internal arrangement of the particles, as proved by the surfaces of fracture, is not however noticed, and the explanation is defective, as it supposes the interior not to have assumed the solid state until the evolution of the heat occurs. If such were the case it would be seen on breaking it in the first instance. The phænomena can only be accounted for by admitting a certain degree of mobility among the particles, and that a second molecular arrangement takes place after the metal has solidified; this may arise from their not having assumed in the first state that direction in which their cohesion was the strongest.

That a very marked and extraordinary alteration in the characters and properties of various substances arises entirely from this change in the position of their component particles, effected either by the communication or abstraction of heat after solidification, there can be no doubt. And these changes are applied to many very important purposes in the arts and manufactures; such as the hardening and tempering of steel, the rolling of commercial zinc, and rendering that metal permanently malleable, the annealing of glass, and a variety of other uses, particularly in crystallization, which might be adduced.

The following experiments were made to ascertain to what extent the emission of latent heat takes place. The melted alloy was poured in a perfectly fluid state on the bulb of a thermometer placed in a small platinum crucible, having a capacity equal to about 70 grain measures of water, and standing in a vessel of cold water or mercury. The thermometer surrounded by the solidified metal and crucible was removed from the cooling medium before it had reached its stationary point, and the greatest decrease of temperature noted. The heat then rose rapidly again, and the maximum effect was registered. The fusing point of the alloy was 202° Fahr.: the following results were obtained:—

Exper.			Fahr.			Fahr.	Diff. Fahr.
1.	thermometer fell to		97°	and then rose to		157°	60°
2.	...	...	94	...	...	149	55
3.	...	...	90	...	...	150	60
4.	...	...	87	...	...	147	60
5.	...	...	104	...	...	156	52
6.	...	...	97	...	...	148	51
7.	...	...	92	...	...	152	60
8.	...	...	104	...	...	155	51

So that in four out of the eight trials a difference of 60° Fahr. was rendered apparent.

In a platinum crucible of larger size the effects were not so marked, 34° Fahr. being the greatest difference obtained; this of course would arise from the greater bulk of the melted metal not exposing comparatively so large a surface to the cooling medium.

XIII. *On the Conversion of Benzoic Acid into Hippuric Acid in the Animal Economy.* *By* Mr. Alfred Baring Garrod, *of University College.*

Read January 18, 1842.

A PAPER has appeared in the Medico-Chirurgical Transactions for last year, and also in the first Number of the Pharmaceutical Transactions, by Dr. Alexander Ure, in which it is stated, that by the internal administration of benzoic acid, or any of its salts, hippuric acid is formed in the system, and is eliminated from the kidneys in the form of a soluble hippurate, and that this hippurate is formed by the benzoic acid uniting with uric acid. It is also stated, that no trace of uric acid, or any of its salts, could be found in the urine after the administration of the benzoic acid.

I have repeatedly performed Dr. Alex. Ure's experiment, swallowing from a scruple to half a drachm of benzoic acid at a time, and have always obtained a copious crop of crystals of hippuric acid, amounting to from fifteen to twenty-nine grains, by the addition of hydrochloric acid to the urine passed about three or four hours afterwards (evaporated or not, according to its state of dilution). These crystals possessed all the characters of hippuric acid, with the crystalline form, the small solubility in cold water and æther, the ready solubility in alcohol, the evolution of nitrogen, and also the odour of the tonquin bean when heated to destruction; and my experiments therefore so far confirm Dr. A. Ure's fundamental ob-

servation. He also mentions another test of hippuric acid, viz. that when evaporated to dryness with dilute nitric acid, and ammonia added, a beautiful purple colour is produced. This is certainly true of the crystals obtained from the urine, but it is not a character of pure hippuric acid. The cause of this colour will be shown presently.

Dr. A. Ure states that no trace of uric acid could be found in the urine; but on examination I have always been able to obtain a distinct trace of uric acid from a drop or two of the urine, by adding a little nitric acid, carefully evaporating, and holding the capsule containing it over ammonia, when a distinct trace of murexide was formed; also, when the dish containing the crystals of hippuric acid is carefully examined, minute grains are found at the bottom, which are uric acid crystals; and on examining the crystals of hippuric acid with the microscope, uric acid crystals are found adhering to them in immense numbers, and this is the cause of the production of the purple colour spoken of, and which has been given as a test of hippuric acid. When the crystals are dissolved in alcohol the uric acid is precipitated, and the hippuric acid crystallized from the alcoholic solution no longer gives the purple colour. On collecting the uric acid from the same quantity of urine, formed on successive days, the same food being taken, one containing about twenty-seven grains of hippuric acid, and the other none, the following results were obtained:—

From $4\frac{1}{2}$ oz. of urine, when no benzoic acid had been taken, uric acid 1·07 grain.

From $4\frac{1}{2}$ oz. of urine, after taking 30 grains of benzoic acid, uric acid 0·96 grain.

Difference in favour of first, 0·11 grain.

In the second experiment also, a small loss might have occurred from the greater washing of the crystals necessary in that experiment. Now if we suppose that uric acid is decomposed to afford the elements necessary to be added to benzoic acid to form hippuric acid, we find that each equivalent of benzoic acid requires the addition of $C_4\,H_6\,O_4\,N$. To obtain the nitrogen, four atoms of benzoic acid would require one atom of uric acid, or half a drachm of benzoic acid would require rather more than ten grains of uric acid. Now the quantity of urine, in the experiment without the benzoic acid, only contained 1·07 grain of uric acid, and yet that quantity was not materially diminished when twenty-eight grains of hippuric acid were found in the urine. It cannot therefore be from the uric acid that the hippuric acid is formed.

If we examine the subject theoretically, it does not seem

probable that such a body as benzoic acid, possessing such feeble affinities, and producing no sensible action on the body when taken, should be able to break up such a stable compound as uric acid; to abstract from the latter the requisite elements for its conversion into hippuric acid. But as hippuric acid is really formed in the urine, from whence does it obtain the necessary addition? The quantity of urea was noticed in several experiments to be deficient; could this be the source? We can find no rational formula for the explanation of the conversion if we suppose it to be from urea alone. We can, it is true, select the elements required; but, as in the last case, we should leave some compound in the system, which cannot be resolved into any known compounds, as ammonia, water, carbonic acid, &c., while from the ready conversion of the benzoic acid into hippuric acid we should expect that the change was one which could easily take place, without the action of any unusual affinities being brought into play. It occurred to me that it might be the lactate of urea, instead of pure urea, which is taken up; and upon comparing the formulæ for hippuric acid, benzoic acid, and the lactate of urea, it appeared that one equivalent of lactate of urea minus three eqs. of water, gave exactly the requisite elements for the conversion of 2 eqs. of benzoic acid into 2 eqs. of hippuric acid. 2 eqs. of benzoic acid + 1 eq. of lactate of urea = 2 eqs. of hippuric acid + 3 eqs. of water.

Hippuric acid (anhydrous)	$C_{18}\ H_8\ O_5\ N_1$
Benzoic acid (Do.)	$C_{14}\ H_5\ O_3$
Difference	$C_4\ H_3\ O_2\ N_1$
Twice the difference . .	$C_8\ H_6\ O_4\ N_2$
Lactic acid	$C_6\ H_5\ O_5$
Urea	$C_2\ H_4\ O_2\ N_2$
Lactate of urea	$C_8\ H_9\ O_7\ N_2$

Lactate of urea $- 3\ H\ O = C_8\ H_6\ O_4\ N_2$.

Now the urea has by MM. Cap and Henry been found to exist in human urine as lactate, and the separation of the elements of water is a change which might be expected to take place in the system under such circumstances. The benzoic acid merely taking up the lactate of urea, and throwing off water, is certainly a more probable occurrence than the destruction of such a stable compound as uric acid.

In analyses for the quantity of lactate of urea, according to the method of Cap and Henry, I found that although I could not obtain it in crystals, yet the quantity in a syrupy state was much reduced after taking the benzoic acid, and the same appeared on forming nitrate of urea from it. I obtained 14 grs.

less of urea in 4½ ounces of urine when the benzoic acid had been taken. In another experiment I obtained 17 grs. less of urea when 30 grs. of benzoic acid had been taken; this is a greater loss than can be accounted for by the formation of the hippuric acid; but this can be referred to the urine, from some accidental circumstance, being of nearly as high specific gravity in this case as when the benzoic acid had been taken. 30 grs. of benzoic acid, swallowed, usually increased the specific gravity of the urine from four to six-thousandths.

From these results two inquiries suggest themselves:—1st, May not hippuric acid be formed artificially out of the body? 2nd, If sufficient benzoic acid were swallowed at such a time when least urea was contained in the urine, would the benzoic acid not cease to be all converted into hippuric acid, part of it then appearing in the urine unchanged?

XIV. *On the Constitution of the Sulphates as illustrated by late Thermometrical Researches.* *By* Thomas Graham, *Esq.*, *F.R.S.*, *&c.*

Read January 18, 1842.

PROF. Hess and Dr. Andrews both apply the results of their late inquiries respecting the heat evolved in combination* to test the accuracy of a view of the constitution of double and acid salts which was published by myself, and arrive, it is remarkable, at opposite conclusions.

The view in question, I may first state, taking the example of double and acid sulphates. Crystallized sulphate of magnesia, and the double sulphate of magnesia and potash, I have represented thus:—

$$Mg\,O,\,S\,O_3\,(H\,O) + 6\,H\,O,$$
$$Mg\,O,\,S\,O_3\,(K\,O,\,S\,O_3) + 6\,H\,O;$$

considering the latter salt to be derived from the former, by the substitution of sulphate of potash for that single atom of water, which is found to be much more strongly attached to the sulphate of magnesia than the other six. This atom of water, which is not basic water, was formerly named *saline* water, to indicate that it is replaceable by a salt; its presence being considered a provision in sulphate of magnesia for the formation of double salts. The water and sulphate of potash are therefore looked upon as equivalent in the construction of the two salts; and the substitution of the salt for the water might therefore be reasonably expected to occur without the evolution of heat.

* Phil. Mag., January 1842.

In accordance with that statement, Dr. Andrews finds that no heat is evolved on mixing solutions of sulphates of magnesia and potash, nor in the formation of any other double salt. On repeating the experiment I found also no heat nor change of temperature on mixing the solutions, although a change of $\frac{1}{20}$th of a degree Fahr. would have been distinctly indicated by my thermometer.

Possibly, however, the double salt may not immediately be formed, and hence no change of temperature at the moment of mixing the two solutions, nor for some time afterwards. To meet this objection, solutions of sulphate of magnesia and of sulphate of ammonia (the last, from its greater solubility, being preferred to sulphate of potash) were made of such a strength that they might be mixed without the precipitation of the double salt immediately occurring, but strong enough to allow a large quantity of the double salt to fall upon stirring the liquid strongly. The solutions were 1546·88 grains of cr. sulphate of magnesia dissolved in so much water as to form 8000 water grain measures, and 613·5 grains oil of vitriol, neutralized with ammonia and made up to 4000 water grain measures. On mixing one ounce measure of the first with half an ounce measure of the second, both exactly at 50°, not the smallest change of temperature could be observed; but as soon as the double salt began to deposit, the temperature rose, and on stirring strongly much salt was deposited, and the temperature rose 5·40° Fahr. On re-dissolving this salt, however, by substituting for the mother liquor an equal bulk of water, the temperature instantly fell 5·85°. Hence the heat which first appeared was produced by the solidification of the double salt, and disappears upon its liquefaction. There is no heat referable to combination of the two salts. The cold on dissolving was always somewhat greater than the heat on precipitating the double salt, in repetitions of this experiment, chiefly, I believe, from the slowness of the precipitation, which requires a minute or two, so that a portion of the heat is lost from contact with the atmosphere, and the whole not observed, while the subsequent solution of the salt being almost instantaneous, the whole fall of temperature is observed. The same experiment was made with a solution of sulphate of zinc, of the same strength as the sulphate of magnesia, and with similar results, only that the fall of temperature, on solution, was somewhat less than that on solidification, namely, as 9°·22 to 9°·67, difference 0°·45 Fahr. This was principally owing to the time required in re-dissolving this double salt being greater than that occupied in precipitating it, three applications of

water being required to re-dissolve the double salt completely, owing to its sparing solubility.

M. Hess's objection is made to the analogous constitution which I have assigned to the bisulphate of potash :—
Sulphuric acid of specific gravity 1·78, $H\,O, S\,O_3 (H\,O)$.
Bisulphate of potash . . . . . $H\,O, S\,O_3 (K\,O, S\,O_3)$.
He maintains that heat is evolved in the formation of a bisulphate, and therefore that the combination is not effected by the equivalent substitution supposed. He mixed sulphate of potash with $H\,O, S\,O_3 + H\,O$, and found heat evolved, but allows that the result here is fallacious, a portion only of the sulphuric acid being converted into bisulphate, while the other portion is diluted by the displaced water of the first portion, and thus heat evolved.

On performing the direct experiment, which M. Hess appears to have neglected, using a saturated solution of sulphate of ammonia, and sulphuric acid of specific gravity 1·256, I obtained, on mixing, 5·4° of cold instead of any heat. But on diluting the sulphate of ammonia with a volume of water equal to that of the dilute acid, a fall of 1·12° occurred. Deducting this from the former, there remains a fall of 3·88° due to the combination of the two salts, sulphate of water with sulphate of ammonia. But this may be explained. The bisulphate of ammonia formed is an anhydrous salt, unlike the double sulphate of magnesia and ammonia, which carries along with it all the water of crystallization of the sulphate of magnesia. But the sulphate of water itself, as it exists in diluted sulphuric acid, is a largely hydrated salt, like sulphate of magnesia. The water of the former, on being set free in the last experiment, absorbs heat, because heat was evolved originally in the combining of this water with the sulphuric acid.

Although certain small corrections on these experiments for changes in capacity for heat of the liquids have been neglected, yet they are sufficient to demonstrate that no heat is evolved in the formation of double sulphates, and also, as appears by the last experiment, that these compounds are formed at once on mixing the solutions of their constituent salts, whether precipitation occurs or not. Sulphate of potash and water are therefore equivalent in the constitution of such salts, or *equi-calorous*, if a term may be coined to express this relation.

XV. *On the Change of Colour in the Biniodide of Mercury.* *By* Robert Warington, *Esq.*

Read February 1, 1842.

IT is well known that when a solution of the iodide of potassium is added to a solution of the bichloride or pernitrate of mercury, a yellow precipitate, passing rapidly to a scarlet, is formed; this is the biniodide of mercury. It is soluble in an excess of either of the agents employed for its production, and if this act of solution be assisted by heat, the biniodide may be obtained, as the solution cools in fine scarlet crystals, having the form of the octohedron with the square base, or its modifications.

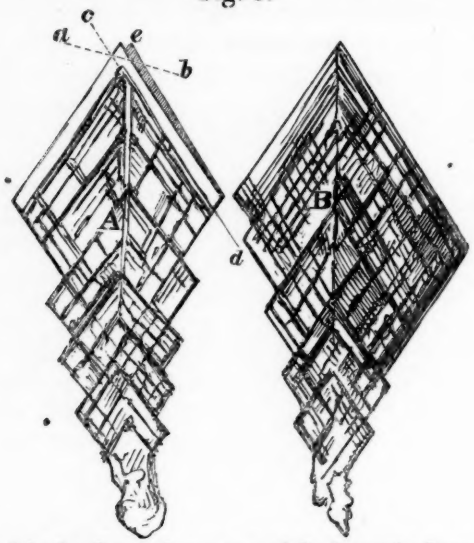
If this precipitated biniodide, in the dry state, be subjected to the action of heat, it becomes of a bright pale yellow colour, fuses into a deep amber-coloured fluid, and gives off a vapour which condenses in the form of rhombic plates of the same bright yellow; these crystals, by any mechanical disturbance, arising from the unequal contraction of their molecules in cooling, from varying thickness in different parts of the same crystal, or from partial disintegration, return again to the original scarlet colour of the precipitate, the change commencing, in the latter case, from the point ruptured, and spreading over the whole of the crystalline mass; they may however be frequently preserved in the yellow state for a great length of time, if sublimed slowly and not exposed to the contact of other substances, which is readily effected by conducting the sublimation in closed vessels, and allowing the crystals to remain in them undisturbed.

The resumption of the scarlet colour has been attributed to an alteration in the molecular arrangement of the crystals, and it was with the view of clearly ascertaining this point that the following microscopic investigations were undertaken.

When a quantity of the precipitated biniodide is sublimed, the resulting crystals are very complicated in their structure, consisting of a number of rhombic plates, of varying size, superposed, sometimes overlapping each other and causing considerable variableness in their thickness, but generally leaving the extreme angle and the two lateral edges clear and well-defined; the annexed sketch, taken by the camera lucida from the field of view of the microscope, will give a better idea of their character. The length of these crystals were about ·015 of an inch in length. On cooling, the first change that is observed is usually a scarlet marking, commencing at the extreme angle and extending gradually inwards, always retaining a perfectly well-defined line in its progress; when this

change has reached as far as the line *a b*, fig. 1, the scarlet

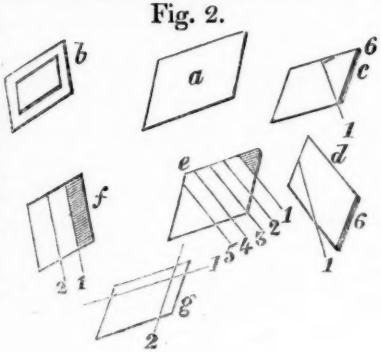
Fig. 1.



line will suddenly shoot along one of the lateral edges, as shown at *c d*, and instantly the whole mass is converted, in a most rapid and confused manner, which the eye in vain endeavours to follow, to the scarlet colour, the crystal being frequently, if detached, twisted and contorted during the transition.

In order to obtain these crystals in a more defined and clearly developed form, a small glass cell was constructed of two slips of window-glass, leaving a space of about the thickness of cartridge paper between the upper and under plates, in which the sublimations could be readily conducted, and the whole of the subsequent changes at once submitted to the microscope; by this means beautifully well-defined and perfect crystals were obtained, having the form of right rhombic prisms, as in the accompanying outlines, fig. 2, *a* and *b*. The following interesting phænomena were then observed: a defined scarlet line of varying breadth would shoot across the crystal, as at 1. *c*, *d*, *e*, *f*, fig. 2, and then gradually spread throughout the whole of its structure, keeping a straight and well-defined line in its onward progress,

Fig. 2.

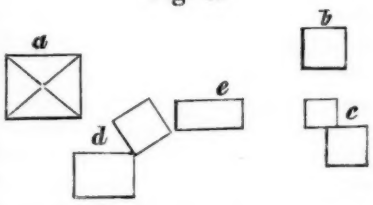


until the whole had undergone the change of colour. Nos. 2, 3, 4, 5 in *e*, and No. 2 in *f*, are the stages which the transition had reached at intervals of observation; in many cases, after the crystal has undergone this metamorphosis, two angles can be distinctly seen, as at *e*, fig. 1, and at times two edges are visible, as at *c* 6 and *d* 6, fig. 2. This observation must of course depend entirely on the position of the crystal to the eye of the observer.

These phænomena prove, I consider, in the most perfect manner, that the change in the colour of this compound arises from the plates of the crystal having been separated from each other, by the means alluded to, in the direction of their cleavages; and in further confirmation of this view, the laminæ so separated may, by the sudden application of heat, be again fused together, and the yellow colour reproduced without materially altering the dimensions of the crystal, a slight rounding of the edges from partial sublimation being the only other concomitant.

When the temperature is raised slowly and the sublimation conducted with great care, a very large proportion of red crystals, having a totally different form, are obtained, the octahedron with the square base, as shown fig. 3, *a*, *b*, *c*, *d*, *e*. If, however, the heat is quickly raised, the whole mass of the sublimed crystals are yellow and of the rhombic form. It is evident from these facts, that the biniodide of mercury has two vapours which are given off at different temperatures, and also that it is dimorphous, which facts have been substantiated by some experiments of M. Frankenheim, who has carefully examined this part of the subject.

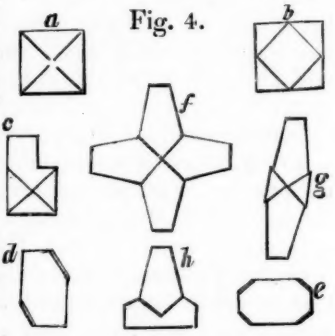
Fig. 3.



From the circumstance that the first effect which occurs in the process for preparing this iodide by precipitation is the production of a yellow powder which passes rapidly through the orange colour to a scarlet, I was induced to submit this phænomenon also to the test of microscopic examination, and with this valuable instrument of research, results were exhibited which could not have been anticipated. As I expected, the precipitate was in small crystalline grains, and the first step of the investigation was to effect its formation in the field of view of the microscope, so as to observe, directly as they occurred, the transitions of colour which have been alluded to, and this was effected by the following means:—A slip of common win-

dow-glass, about three inches long by one and a half wide, and having a very narrow slip attached on one of its edges, so as to act as a ledge, was taken, and a drop of the salt of mercury employed placed on it; this was then covered with a small piece of extremely thin glass, about one inch long by half an inch wide, and the whole carefully adjusted to focus in the field of the instrument; the iodide of potassium was then introduced by capillary attraction between the glasses. The instant the solutions came in contact, a myriad of pale-yellow crystals, having the same rhombic form as those obtained by sublimation, formed in a curved line across the field of view and extended slowly downwards; by the strong transmitted light these minute crystals appeared colourless; but when viewed by reflected light, the pale yellow colour was readily apparent. After a short interval a very extraordinary change commenced; the crystals, which had been perfectly sharp and well-defined, became ragged at their edges, as though some dissolving action were going on, gradually decreased in size, and at last disappeared altogether; but as this act of solution progressed, numbers of red crystals made their appearance, forming across the field and following at a regular distance the yellow crystals as they disappeared, and occupying their place. These red crystals, which appear to be formed by the disintegration through the medium of solution, if I may be allowed the expression, from those first produced, had the form of the octohedron with the square base, exactly similar to those procured by careful sublimation at a low heat, only modified in the most beautiful manner. Some few of these are sketched in the forms, *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, fig. 4. When either the salt of mercury or the iodide of potassium, employed in the production of the biniodide of mercury, was in excess, another curious act of disintegration took place; the red crystals in fig. 4 were slowly dissolved, a property mentioned in the first part of this paper, the first act of solution commencing apparently by the disjunction of the crystals *a*, *b*, *c*, *f*, *g*, *h*, at the lines of marking, these lines being at first bright red, and gradually deepening in colour when the act of solution commenced, and at last perfect separation taking place, so that the light could be seen between the compartments. At times the field would become dry from

Fig. 4.



evaporation, and some of the yellow rhombic crystals which had not been dissolved, prior to the formation of the octohedra with the square base, were observed with scarlet lines on them similar to the first act of transition in the sublimed crystals, as shown at *g* 1 and 2 in fig. 2.

By polarized light the appearances now described were beautiful beyond all description, the yellow crystals presenting the most superb and brilliant colours, varying in hue with the varied thickness of the crystalline plate, and in the dark field having the appearance of the most splendid gems the imagination can conceive: the red crystals do not appear to be affected by polarized light, so far as the display of colour is concerned.

The magnifying powers used in these investigations were, for the experiments on the sublimed crystals, 200 times linear measurement or diameters; in the precipitated compound, 620 diameters.

XVI. *On a new Oxalate of Chromium and Potash.* By Henry Croft, *Esq.*

Read February 15, 1842.

IT is well known that in 1830 Wilton Turner accidentally discovered a salt composed of oxalate of the oxide of chromium and oxalate of potash. Its curious optical properties have been examined by Brewster. Gregory also discovered the same salt independently, and proposed a much better method for obtaining it than that used by Turner, which consisted in adding oxalic acid to a solution of bichromate of potash until effervescence ceased; the solution became deep green or black, and on evaporation yielded beautiful crystals of the black salt. Gregory supposed it to consist of 3 equivalents of oxalic acid, 2 of potash, 1 of oxide of chromium, and 6 of water. Its true composition, $3\,(KO, C_2O_3) + Cr_2O_3$, $3\,C_2O_3 + 6\,HO$ has been shown by Graham and Mitscherlich, who have also prepared a number of salts similarly constituted.

On attempting to prepare the black salt by Turner's method I could never completely succeed, but obtained in its stead, when a very concentrated hot solution of the bichromate was employed, a red granular precipitate, which proved to be a new salt, and forms the subject of the present notice.

Perhaps the best method of preparing it is that above described, viz. to employ as concentrated a solution of the bichromate as possible, in which case the salt crystallizes out on cooling. The precipitated salt must be redissolved in a small

quantity of water and allowed to crystallize. It is however one of the most difficult salts to crystallize that is known: in nine cases out of ten it separates in the form of a somewhat granular bluish gray powder, and it appears to be only under particular circumstances that it will crystallize well, which, however, I was not able to discover. It does not seem to crystallize any better by spontaneous evaporation than out of a very concentrated solution; it seems however to form more regularly in warm air, as in summer. The best crystals are generally formed on the surface of the solutions: they are very minute, in the form of triangular plates; when the crystals form a mass at the bottom of the liquid the plates are thicker, but their form is indistinguishable. The salt is of a deep red colour by reflected as well as by transmitted light; the solution is green, or even black (when concentrated) by reflected and red by transmitted light. The solution when at a boiling temperature remains red, as is seen best by candle-light: the same is the case with the solution of the black salt, which shows that the purple oxide of chromium contained in these salts is not converted by a boiling heat into its green modification; the purple oxide must, however, as is well known, be first brought into combination with the oxalic acid, for the black salt can never be obtained by dissolving *green* oxide of chromium in binoxalate of potash.

A solution of caustic potash added to a solution of the red salt turns it bright green, but causes no precipitate until boiled, when the greater part of the oxide of chromium is thrown down. Carbonates of the alkalies partly change the colour in the same manner, but do not precipitate the oxide so readily. Ammonia causes no precipitate, nor does chloride of calcium, owing to the formation of Dingler's oxalate of chromium and lime; when ammonia is added a green precipitate containing oxide of chromium is formed.

This salt contains a large quantity of water of crystallization, which can only be driven out by a strong heat, as is also the case with the black salt (Graham). It loses about 15–16 per cent. at 100° cent., and 19 per cent. at 200° cent. The last portions of water can only be driven out at 300° cent. Near this point the salt begins to be decomposed, and consequently the determination of the water is rendered somewhat difficult.

				per cent.
0·9986	gramme of salt lost	0·2638	water =	26·42
0·7481	... ...	0·1965	... =	26·27
0·8971	... ...	0·2532	... =	28·22

The determinations of the oxide of chromium and the potash were performed in the following manner. The salt was heated red-hot: in this opeattion great care must be taken,

for the salt possesses the curious property of decomposing with considerable violence (without explosion) into a green powder, which, unless the heat is applied very gradually, is forced out of the crucible, and the analysis is thus lost. When the temperature is raised gradually the crystals retain their form, but become of a bright dark green colour: as soon as the decomposition of the oxalates commences they fall into a light green powder, which when stronger heated becomes brown. In closed vessels carbonate of potash is formed; in open ones, when the heat is continued for a length of time, chromate is produced. This chromate must be extracted by water, reduced, and the oxide of chromium precipitated by ammonia: in this operation, however, it is better to evaporate the ammoniacal solution to dryness, as the ammonia always dissolves a small quantity of the oxide. This method is preferable to that usually employed (Heinrich Rose's Analytical Chemistry): the ammoniacal and potash salts must be dissolved out, evaporated, the ammonia driven off, and the potash determined either as chloride or by means of platinum.

The oxalic acid may be determined by boiling the salt with sulphuric acid, as proposed by Prof. Graham.

The salt being excessively difficult to crystallize, it seldom happens that a perfectly homogeneous substance can be obtained for analysis: the method of analysis is moreover somewhat complicated, and consequently the analyses do not agree so perfectly as could be desired.

	I.	II.	III.	IV.	V.	VI.	
Cr_2O_3	21·80	21·83	23·11	22·05	21·10	24·11	
KO	13·18	13·11	12·22	12·92			
C_2O_3	37·00	36·98					40·89

The water as obtained by other experiments, is

H O	26·42	26·27	28·22

The most plausible formula is $KO, C_2O_3 + Cr_2O_3, 3\,C_2O_3 + 12\,HO$.

C_2O_3	4	1811·50	38·098
Cr_2O_3	1	1003·63	21·107
K O	1	589·92	12·405
H O	12	1349·75	28·390
		4754·80	100·000

This differs from the black salt in containing one atom of basic oxalate instead of three. It may be said to be related to the black salt in the same way as metaphosphates are to phosphates. It is evident, therefore, that if we add two atoms of oxalate of potash to one atom of the red salt, we ought to obtain the black salt, which is indeed the case.

2·37 grammes of red salt were mixed with 1·15 gr. of oxalate of potash (these are the atomic proportions), the solution boiled and evaporated, they yielded 3·119 grs. of the black salt in good crystals, and perfectly pure: according to theory it ought to have given 3·070. The weight of the black salt must be equal to that of the red salt, *plus* two atoms of anhydrous oxalate of potash, *minus* six atoms of water. The agreement of the experiment with the calculation speaks for the correctness of the above formula, in which one might, perhaps, otherwise not place so much confidence.

The constitution of this salt led me to consider the theory of its formation, and also that of the black salt, more particularly as in employing the known formulæ for making the black salt I always obtained it mixed with other bodies.

In forming the red salt from bichromate of potassa, 7 atoms of oxalic acid are required. $K\,O$, 2 $Cr\,O_3$ and 7 $C_2\,O_3$ = $K\,O$, $C_2\,O_3$ + $Cr_2\,O_3$, 3 $C_2\,O_3$ and 3 $C_2\,O_3$ + 3 O, or 6 $C\,O_2$. On mixing the two substances in this proportion I obtained perfectly pure red salt. It is evident that seven atoms of oxalic acid, either free or in combination with potash, must be used in making the black salt. None of the numbers in the formulæ given for preparing the black salt agree with this.

Dr. Gregory gives 190 parts bichromate of potash, 157·5 parts crystallized oxalic acid, and 517 parts binoxalate of potash; that is, one atom of the bichromate, two atoms oxalic acid, and three of binoxalate of potash; on trying these numbers I obtained a mixture of black salt with oxalate and chromate of potash.

Prof. Graham proposes one part of bichromate, two of binoxalate, and two of crystallized oxalic acid. In these proportions a large quantity of chromate of potassa remains undecomposed, which requires, if 19 grains bichromate, 23 grains binoxalate, and 16 grains crystallized oxalic acid be taken, exactly 36 grains of crystallized oxalic acid to effect its perfect decomposition, and making the whole quantity of oxalic acid 52 grains.

According to the formula which I would propose, there are required

19 grains bichromate of potash
23 ... oxalate of potash
55 ... crystallized oxalic acid.

If the salts be taken in these proportions, nothing but black salt is obtained; it is however better to evaporate the whole to dryness and then re-dissolve.

I have not been able to obtain an intermediate salt, namely, 2 $K\,O$, $C_2\,O_3$ + $Cr_2\,O_3$, 3 $C_2\,O_3$. This, if it exists, ought to

be produced from two atoms chromate of potash, and eight atoms oxalic acid : I obtained, however, oxalate of potash and red salt.

A similar salt may probably exist with oxide of iron, but it does not crystallize. On dissolving sesquioxide of iron in quadroxalate of potash a solution is obtained, which dries to a brown gummy mass without traces of crystallization.

XVII. *Some additional Observations on the Red Oxalate of Chromium and Potash.* By Robert Warington, *Esq.*

Read May 17, 1842.

HAVING in the year 1832 obtained this salt by the same method as that described by Mr. Croft, namely, in the endeavour to prepare the dark blue oxalate of chromium and potash by the process originally given by its discoverer Dr. Wilton Turner, and having in my possession some crystals of a much larger size than those usually obtained, I was induced to avail myself of the kind offer of Professor Miller of Cambridge, "to determine the form of any crystalline products that the members of the Society might obtain in their researches," and have great pleasure in laying before the Society the following letter and measurements:—

"St. John's College, Cambridge, April 25, 1842

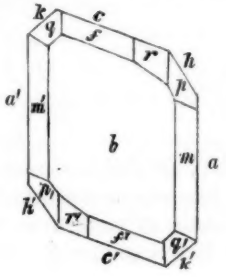
"Dear Sir.—The crystals of the oxalate of chromium and potash are represented in the accompanying figure. The numbers expressing the angles between normals to the faces must be considered as rough approximations only, for although I measured all the measurable crystals you sent me, the variations of the angles between corresponding faces showed that the crystals were by no means so perfect as could be wished.

"The angles given are however abundantly accurate for the purpose of identifying the substance. One of the crystals was a twin, the face (*a*) being the twin face or the face with respect to which the two individuals were symmetrically situated.

"*Oxalate of Chromium and Potash-system—Oblique prismatic.*

"*Angles between normals to the faces of the crystal.*

a c	70°	45′	*c p*	50°	40′
a h	33	2	*c m*	77	32
c h	37	43	*a r*	61	0
b p	53	13	*a f*	78	30
c k	59	16	*a′ q*	63	50
a p	47	49	*b f*	37	40
a m	49	5			



"The faces *a p r f q* are all in one zone; *h p b* are in one zone; *k q b* are in one zone; *a h c k* are in one zone. The other zones are sufficiently well indicated by the parallelisms of the edges.

"The symbols of the faces are,—*a* (100), *b* (010), *c* (001), *h* (101), *p* (111), *q* (111), *f* (011), *m* (110), *k* (101), *r* (112).

"I remain yours faithfully,

"W. H. Miller."

These crystals, submitted to measurement by Professor Miller, were obtained by slow spontaneous evaporation: the difficulty of procuring this salt in crystals of any size has been fully pointed out by Mr. Croft.

I have only one observation which does not coincide with Mr. Croft's statements, but which, however, confirms in a great measure the results of his analysis; I allude to the statement that these double salts of chromium cannot be formed by the direct combination of their ingredients. The process which I have followed has been to digest the hydrated oxide of chromium in a mixed solution of oxalic acid and oxalate of potash in the proportions indicated by analysis, and when it ceases to dissolve the oxide, to decant the clear solution and allow it to crystallize. By the same means the analogous salts of soda and ammonia have been obtained, but not in crystals sufficiently large for measurement, as also other double salts of chromium. To prepare the hydrated oxide of chromium, the best and most œconomical process that I have found, is to take 150 grs. of the bichromate of potash and 200 grs. of liquid sulphuric acid, oil of vitriol, these proportions being nearly in the ratio of their atomic weights, so that the chrome alum, sulphate of the green oxide of chromium and potash, may be formed; the deoxidation of the chromic acid is easily effected by the addition of a little sugar and boiling the solution. When the deoxidation is complete, the green oxide may be precipitated by ammonia or by a carbonated alkali, and only requires to be well washed to remove all trace of alkali or saline matter.

XVIII. *On the Preparation of Cyanide of Potassium, and on its Applications. By Prof.* Liebig *of Giessen. Translated by* Mr. W. Francis, *and communicated through him by the Author.*

Read March 1, 1842.

ONE of the best methods of preparing the cyanide of potassium is founded on the decomposition of the yellow prussiate of potash at a red heat; it is, however, attended with much inconvenience, and a third part of the cyanogen

contained in the salt is lost. Considered as a compound of two atoms of cyanide of potassium with one atom of protocyanide of iron, the former undergoes no change on exposure to a red heat, while the latter is decomposed into carburetted iron with evolution of nitrogen gas. The carburet of iron, like a sponge, imbibes the fused cyanide of potassium, to obtain which free from iron and without loss a solvent such as alcohol is required. As the cyanide of potassium is possessed of properties which render it highly valuable as a means of reduction and separation in chemical analysis, I have endeavoured to simplify the preparation of it. When eight parts of the yellow prussiate are sharply dried (slightly roasted) on a hot plate of iron, then finely powdered and mixed well with three parts of dry carbonate of potash, and thrown at once into a Hessian crucible previously heated to redness, and kept at that temperature, the mixture fuses into a brown magma with a lively evolution of gas. After a few minutes, when the fluid mass has become red-hot, its dark colour is seen to become brighter, and on continued fusion the salt becomes clear and of an amber-yellow tint. If from time to time a hot glass rod be immersed in it, the adhering mass on cooling is at first brown, afterwards yellow, and at last, towards the close of the operation, clear and colourless as water, and solidifies into a shining white crystalline mass.

During the fusion brown flocks are seen floating in the fluid mixture, which subsequently unite into a spongy mass and assume a light gray colour. If the crucible be now removed from the fire and allowed to cool somewhat, the gray powder generally settles entirely at the bottom; this is facilitated by stirring once or twice with the glass rod. The fused mass may now be easily poured into a warm porcelain dish without a particle of the sediment accompanying it. This mass consists of two combinations, of which the cyanide of potassium forms the chief portion; the other compound is the cyanate of potash, in the proportion of five of the former to one of the latter. The reaction in the fusion of the yellow prussiate with carbonate of potash is as follows:—at the commencement, the protocyanide of iron of the ferrocyanide is decomposed, and forms cyanide of potassium with the potash of the alkaline carbonate, and the protocarbonate of iron, which is deprived of all its oxygen at a higher temperature by the cyanide of potassium. In consequence of this reduction, cyanate of potash and pure metallic iron are obtained.

Let us suppose in the mixture two atoms of ferrocyanide of potassium and two atoms of carbonate of potash, we then have as sum of the constituents,

Ferrocyanide of potassium. Carbonate of potash.
$Cy^6\ Fe^2\ K^4$ and $K^2\ O^2 + 2\ C\ O^2 = Cy^6\ Fe^2\ K^6\ O^2$ and $2\ C\ O^2$.

And we obtain after fusion,

Cyanide of potassium.	Cyanate of potash.	Iron.	Carbonic acid.
$Cy^5\ K^5$	$Cy\ O + K\ O$	Fe^2	$2\ C\ O^2$.

From two atoms of the ferrocyanide of potassium we thus obtain five atoms of the cyanide, that is, one-fourth more than by fusing it alone. The cyanate of potash mixed with it has no injurious influence in any one of its applications. The presence of cyanate is readily detected by the effervescence caused from the escape of carbonic acid on the addition of an excess of acid, and an ammoniacal salt is afterwards found in the liquid. The explanation given above of the formation of the cyanide of potassium under the conditions described is not absolutely correct, as the protocarbonate of iron previous to its reduction is decomposed into carbonic acid, carbonic oxide, and the proto-peroxide (black oxide) of iron, at the expense of which an undeterminable quantity of cyanate is formed more than the formula indicates. The metallic iron precipitated and the sides of the crucible are covered by cyanide of potassium, to obtain which it is best to remove with cold water all that is soluble, and to warm the solution with some sulphuret of iron, which easily dissolves in it. The cyanide of potassium is thus obtained, on evaporation, again in the form of ferrocyanide, and sulphuret of potassium remains in the mother ley.

Preparation of Hydrocyanic Acid.—The cyanide of potassium of the preceding process is much better adapted for the preparation of prussic acid than the ferrocyanide; a larger quantity is obtained, and the distillation is easier. It is well known, that on distilling the yellow salt with sulphuric acid a bluish-white powder is deposited, a combination of cyanogen, potassium and iron, the composition of which is analogous to that of cyanide of iron and zinc, and is represented by the formula $2\ Cfy + \left\{\begin{matrix} K \\ 3\ Fe \end{matrix}\right.$; where $Cfy = Cy^3\ Fe$.

From the formation and composition of this body, it results, that not more prussic acid can be obtained from five atoms of the ferrocyanide, which contain fifteen atoms of cyanogen, than from nine atoms of cyanide of potassium, which only contain nine; the other six atoms remain in the bluish-white precipitate. When the yellow salt is converted, according to the above method, into cyanide of potassium, twelve and a half equivalents of hydrocyanic acid are obtained from five atoms of the ferrocyanide, or three and a half equivalents more.

It is usual to take so much sulphuric acid to decompose one atom of the yellow salt as will suffice to form with the alkali the bisulphate of potash: on employing cyanide of potassium, only one atom of the hydrate of the acid is requisite. Equal parts of the cyanide of potassium and proto-hydrate of sulphuric acid are the best proportions for preparing hydrocyanic acid; that quantity of sulphuric acid exactly suffices to form with the whole of the potash a neutral sulphate, and with the ammonia originating from the decomposition of the cyanate, the bisulphate of oxide of ammonium. The cyanide of potassium is dissolved in double its weight of water, and the sulphuric acid diluted with three times its weight of water slowly added in small portions: previous to each addition the effervescence must have subsided.

Preparation of Cyanate of Potash.—The cyanide of potassium, prepared according to the method above described, is an excellent means of procuring easily and with very little loss the cyanate of potash. It is most advantageous for this purpose to make use of common litharge which has been previously heated slightly. The cyanide of potassium is fused in a Hessian crucible, and the powdered litharge thrown from time to time into it; the oxide of lead is instantaneously reduced to metal, which at first remains as a fine powder mixed with the cyanate formed, but melts with greater heat into a regulus. The fluid mass is poured out, and the salt, which is nothing else than cyanate of potash, being finely pounded, is boiled so long with alcohol as crystals are obtained. The crystallization of the cyanate of potash salt from alcohol is not requisite in the application of that salt to the preparation of urea.

Cyanide of Potassium as a reducing agent.—It is difficult to conceive with what extreme facility the cyanide of potassium deprives certain metallic oxides and sulphurets of their oxygen and sulphur, for it approaches nearest in that respect to pure potassium. The process of preparation of cyanide of potassium and that of the cyanate afford two instances of this reducing power; the iron remains either as powder mixed with the fused cyanate, or its particles aggregate together and form a spongy mass. A process might be founded on this reduction for determining in the dry way the amount of metal in an iron ore. When a weighed quantity of the ore is exposed with a mixture of cyanide of potassium and carbonate of potash in a porcelain crucible to a strong red heat, the alumina and silica go into the slag, from which the reduced iron can then be separated by cold water and weighed. The protoxide of manganese is not reduced by the cyanide of potassium; this, when contained in the ore, must be determined by a separate operation. When oxide of copper is sprinkled on

melting cyanide of potassium, it is immediately reduced with evolution of heat and light; after washing, a regulus of pure metallic copper is obtained. The reduction proceeds most beautifully with the oxides of tin and antimony. At a low red heat the oxide of tin is converted into a bright regulus, which may easily be separated from the slag. The oxide of antimony and antimonious acid may be reduced in the same way to the metallic state. All these reductions ensue at a low red heat scarcely visible in daylight, which consequently has the advantage, that not a trace of the reduced metal is lost by volatilization. Sulphuret of tin and sulphuret of antimony are reduced by gently melting them with cyanide of potassium before the blowpipe or in the porcelain vessel, with the same ease as their corresponding oxides; the slag then contains the sulphocyanide of potassium. The cyanide of potassium does not only possess this reducing power in the dry way, but likewise in a dissolved state: mixed with a solution of alloxan, a heavy crystalline precipitate, scarcely soluble in water, of dialurate of potash, is formed in a few seconds.

Cyanide of Potassium as an agent of separation in Quantitative Analysis.—Nickel, cobalt and manganese are so nearly related in their properties, that their separation is attended with great difficulties. In one single form of combination only does nickel differ from cobalt to such an extent that this might be used as an absolute means of separation.

The oxide, protochloride, or any salt of cobalt warmed with cyanide of potassium and an excess of hydrocyanic acid, is converted into the percyanide of cobalt and potassium (the cobalti-cyanide of potassium), the aqueous solution of which, according to the observation of L. Gmelin, does not undergo the slightest decomposition from boiling with hydrochloric, sulphuric or nitric acid.

The oxide of nickel and its salts are thrown down by the cyanide of potassium; this precipitate dissolves in an excess of the precipitating agent of a yellow colour; and the double compound of cyanide of nickel and cyanide of potassium, although not decomposed by acetic acid, is perfectly so by dilute sulphuric acid, and the cyanide of nickel again precipitated.

When a mixture of a cobalt and nickel salt containing free acid is treated with an excess of cyanide of potassium, so that the precipitate formed is redissolved, there are in solution free hydrocyanic acid, cyanide of potassium, cyanide of nickel, and the protocyanide of cobalt; the latter changes immediately, on being slightly warmed, into the cobalti-cyanide of potassium; if now dilute sulphuric acid be added in the cold, three cases present themselves.

If the cobalt and nickel in solution are in the proportion by weight of two cobalt to three nickel (quantities which correspond to their atomic proportions in the cobalti-cyanide of nickel), the precipitate produced is cobalti-cyanide of nickel, and is of a bluish-white colour. The filtered liquid contains not a trace of cobalt or nickel.

If the solution contains less nickel than corresponds to the above proportions, there remains in solution a certain quantity of cobalti-cyanide of potassium, and the precipitate is still cobalti-cyanide of nickel.

If there is more nickel present in the solution, the precipitate is a mixture of cyanide of nickel and cobalti-cyanide of nickel.

In the first and second cases, the precipitate produced by dilute sulphuric acid is boiled so long with the acid fluid in a vessel until not a trace of hydrocyanic acid is observed to escape (or it may be evaporated to dryness in a water-bath), and then slightly warmed with an excess of carbonated or caustic potash; the cobalti-cyanide of nickel is decomposed by this into (1) pure oxide of nickel, or the carbonate, which is washed on a filter, dried and weighed, and (2) an alkaline liquid which contains the whole of the cobalt. The latter is evaporated to dryness, some nitre being added to it, and the residuum ignited. On being treated with water, the oxide of cobalt remains behind.

This method is applicable in all analyses of cobalt ores in which the amount of cobalt predominates. For nickel ores, in which the quantity of cobalt amounts merely to a minimum, the following precaution must be attended to:—a somewhat considerable excess of muriatic acid must be taken to precipitate the cyanides dissolved in the cyanide of potassium, and the mixture must be kept boiling at least one hour.

The precipitate contains in this case cyanide of nickel intermixed, which is decomposed by potash into cyanide of potassium and oxide of nickel; this cyanide of potassium retains however another portion of nickel in solution. On boiling the precipitate with muriatic acid, the cyanide of nickel is decomposed into chloride of nickel and hydrocyanic acid, which last is removed by boiling, and no longer prevents the entire precipitation of the nickel. The cobalti-cyanide of nickel is not attacked by boiling hydrochloric acid, so that a complete solution cannot be expected when any quantity of cobalt is present. When the smell of hydrocyanic acid is no longer perceptible, the boiling has continued long enough.

Experiments made to separate the solution of the two cyanides in cyanide of potassium by boiling with peroxide of

mercury, gave less certain results. The following points must be attended to in this process:—as the cyanide of potassium used contains a certain quantity of cyanate of potash, a portion of an ammoniacal salt originates on its decomposition by a mineral acid; accordingly, after boiling and the addition of caustic potash, ammonia is set free, which retains some oxide of nickel in solution. This nickel is entirely thrown down by boiling for a few minutes, or by a larger addition of potash.

The same method may be followed for the separation of manganese from cobalt, only in this case a complete solution of the precipitate produced by the addition of the cyanide of potassium to the mixture of the two metallic salts cannot be expected; the greater portion of the protocyanide of manganese remains undissolved. The residue is filtered, and the liquid treated as if cobalt and nickel were to be separated.

The cyanide of potassium is not less applicable with advantage for the separation of the oxide of chromium from protoxide of iron. A mixture of the two is previously saturated with sulphuretted hydrogen, to be certain that the iron is contained in the liquid as protoxide (an addition of a few drops of the sulphuret of ammonium answers the same purpose), and then thrown down by cyanide of potassium, and an excess of the latter added. The iron then dissolves immediately as ferrocyanide of potassium, while the oxide of chromium is left behind. In many cases the cyanide of potassium can be employed to advantage in separating iron from alumina (little iron from much alumina), as the protoxide as well as the sulphuret of iron are so easily soluble in that salt, while alumina is perfectly insoluble. The cyanide of potassium well deserves to be studied as a general agent of separation. Unfortunately the composition of the numerous double compounds it forms with other cyanides is only imperfectly known, while their relation to mineral and vegetable acids is wholly unknown, so that the entire investigation must necessarily be repeated.

XIX. *On the Preparation of Artificial Yeast.* *By* George Fownes, *Ph.D.*

IT often becomes a matter of great practical importance to have it in our power to excite the vinous fermentation under circumstances in which ordinary yeast cannot be obtained. In making bread, for example, although the use of yeast may be avoided by employing what is called "leaven," or dough which has already become sour and partly putrefied by spon-

taneous change—a practice which has been followed from the most remote antiquity, and is still occasionally in use—the bread so made is always to be distinguished by a peculiar sour and nauseous taste and smell, and can never bear comparison with that fermented by yeast.

The object of the present notice is to point out a method by which yeast of the most unexceptionable quality can be artificially produced at will. I am aware that some substitute for ordinary ferment in brewing has long been known to certain persons, who go about the country and impart their secret to those who are willing to purchase it: of the nature of this preparation I am ignorant, and a reference to systematic chemical works will suffice to show, that whatever it be it has never been made public.

On turning to Berzelius, it will be found stated*, that although the reproduction, as it were, of yeast, the conversion of a small into a large quantity, is a very easy thing, yet to produce that substance from the beginning is very difficult. He describes a process for this purpose on the authority of Dr. Henry, and which consists in taking a strong infusion of malt, saturating it with carbonic acid, and then exposing it for some days to the proper fermenting temperature, when a small quantity of yeast is gradually formed and deposited, which may, by various contrivances, be made to give origin to a larger. I shall have occasion to notice presently the behaviour of a malt infusion when left to itself at a temp. of 70° or 80° F. for some time, and to show that the addition of carbonic acid is wholly unnecessary.

The principle of induced chemical action, which Liebig has assumed to explain a great number of those extraordinary phænomena to which Berzelius gave the term "Catalysis," and which principle has been so fully confirmed, and even, perhaps, extended by the late valuable researches of MM. Boutron and Fremy on the formation of lactic acid, serves to solve this difficulty, as it will doubtless many others of far greater magnitude and importance. It has been shown that "the kind of chemical change going on in the decomposing azotized body or ferment, determines the kind of decomposition which shall occur in the neutral ternary substance, subject to its influence;" that diastase, for example, according to its peculiar condition, whether fresh from the germinated grain, slightly putrefied, or in a still more advanced state of that change, possesses the singular power, in the first case, of changing starch into dextrin, and ultimately into grape sugar; in the second, of causing the conversion of sugar into lactic

* Lehrbuch, vol. viii. 89. foot note, third edition.

acid; and in the third and last, of exciting the vinous fermentation.

Now if common wheaten flour be mixed with water to a thick paste, and exposed, slightly covered, to spontaneous change in a moderately warm place, it will be observed to run through a series of changes which seem very closely to resemble those described by MM. Boutron and Frémy in the case of diastase.

About the third day of such exposure it begins to emit a little gas, and to exhale an exceedingly disagreeable sour odour, much like that of stale milk; after the lapse of some time this smell disappears, or changes in character, the gas evolved is greatly increased, and is accompanied by a very distinct and somewhat agreeable vinous odour: this will happen about the sixth or seventh day, and the substance is then in a state to excite the alcoholic fermentation.

A quantity of brewers' wort is next to be prepared in the usual manner, by boiling with hops; and when cooled to 90° or 100°, the decomposed dough before described, after being thoroughly mixed with a little tepid water, is added to it, and the temperature kept up by placing the vessel in a warm situation. After the lapse of a few hours active fermentation commences; abundance of carbonic acid, having its usual agreeable pungent smell, is disengaged, and when the action is complete and the liquid clear, a large quantity of excellent yeast is found at the bottom, well adapted to all purposes to which that substance is applied.

In one experiment the following materials were used:—a small handful of ordinary wheat flour was made into thick paste with cold water, covered with paper, and left seven days on the mantel-shelf of a room where a fire was kept all day, being occasionally stirred: at the end of that period three quarts of malt were mashed with about two gallons of water, the infusion boiled with the proper quantity of hops, and when sufficiently cooled, the ferment added. The results of the experiment were, a quantity of beer, not very strong, it is true, but quite free from any unpleasant taste, and at least a pint of thick barm, which proved perfectly good for making bread.

It appears to me that this simple plan would enable distant residents in the country, and settlers in the colonies, to enjoy the luxury of good bread when a little malt could be got—a very easy home manufacture from grain of any kind: the hops might probably be omitted when the yeast alone was the object.

A moderately strong infusion of malt which has not been boiled, suffered to stand in a warm place for some days,

speedily becomes sour and turbid, and begins to evolve gas; this change rapidly progresses, carbonic acid is given out plentifully, and a deposit of thick insoluble whitish matter formed, which readily excites fermentation in a dilute solution of sugar; the supernatant liquid contains alcohol, acetic acid, and, I believe, lactic acid.

When wort which has been boiled and hopped is set aside to decompose spontaneously, the change it undergoes appears to depend very much upon its strength. When weak, three or four days elapse before anything is noticed; a scum then collects upon the surface, and a brown flocculent substance is thrown down, which is incapable of exciting fermentation in a solution of sugar, while the liquid gives off a flat, offensive smell. If the infusion experimented on be stronger, then the change is different: the liquid becomes turbid from the separation of a yellowish adhesive substance, a good deal of gas is very slowly emitted, alcohol is formed, and the deposit at the bottom of the vessel proves a pretty active ferment to sugar. The acidity of the liquid is but trifling, and its smell is somewhat disagreeable. These differences in the behaviour of boiled wort may also depend upon the quantity of hops added and the length of time during which the ebullition had been continued.

The effect produced in a spontaneously fermentable liquid by vegetable acids, or acid salts, such as cream of tartar, is a curious subject of inquiry. From an experiment made upon some wort, it appeared not improbable that the result of such addition showed an interference in the formation of lactic acid. We know that when the juice of grapes, or currants and gooseberries, is exposed to the air, the vinous fermentation is set up apparently at once; whereas in an unboiled infusion of malt, which is destitute of these substances, lactic acid seems to be first formed, although ultimately the two fermentations go on together.

I stated, when speaking of the spontaneous decomposition of wheaten dough, that an acid state preceded that in which it became an alcoholic ferment; and if in this condition it be mixed with a dilute solution of common sugar, and the whole kept warm for several days, it furnishes a sour liquid which is rich in lactic acid, and from which white crystallized lactate of zinc is easily prepared. There is a tendency in the liquid to run into the alcoholic fermentation, and to produce vinegar by a subsequent change, but still the quantity of lactic acid so formed is very considerable.

Common wheat-gluten then in its mode of decomposition strikingly resembles diastase; like that substance it runs in

succession through two different dynamic conditions; it is successively a lactic acid and an alcohol ferment; is it too much to expect that it might by proper means be detected in a third condition, namely, as a "sugar ferment," like diastase itself in the state in which it exists in malt? Is it not possible that diastase, as a definite proximate principle, has no more existence than yeast; that its powers are purely dynamic, and that it is, in short, nothing more than the gluten of the seed in one of its earliest stages of decomposition? This is an interesting inquiry, but its prosecution will be somewhat difficult from the rapidity with which these changes succeed each other; it must be remembered that no one has yet succeeded in getting diastase in a state fit for analysis.

XX. *On some Salts of Cadmium.* By Henry Croft, *Esq.*

Read May 17, 1842.

CHLORIDE of cadmium is exceedingly soluble in water and cannot be obtained in good crystals. If it be treated with a solution of ammonia, it is not at first dissolved; but on heating, the white powder which is at first formed, disappears, and on cooling a granular crystalline powder falls out of the solution. It is a compound of the chloride with ammonia. By heating, it loses 16·63 per cent of ammonia; according to the formula $Cd\,Cl + H^3\,N$ it would lose 15·12; the excess obtained is owing to a portion of the chloride being decomposed when sal-ammonia is evolved. The proof of this is that the heated salt is not perfectly soluble in water.

If dry ammonia be passed over pulverised anhydrous chloride of cadmium, the powder increases greatly in bulk under evolution of heat. At first there is but little action, and the stream of ammonia must be passed over the salt for some time before violent absorption takes place. 1·276 gr. absorbed 0·6835 gr. of ammonia, or 100 parts absorbed 53·56; according to the formula $Cd\,Cl + 3\,N\,H^3$ it would be 56·47: the difference probably arises from the great increase in bulk which the salt undergoes, and which may prevent the ammonia reaching every particle.

This compound loses ammonia when exposed to the air; when it has ceased to smell of ammonia, it is converted into the first-mentioned compound, viz. that containing one atom of ammonia.

Bromide of cadmium crystallizes in long prisms somewhat similar to nitre; it loses its water of crystallization when exposed to a dry atmosphere: 2·422 grs. lost, when heated to

100°, 0·5075 gr. of water; that is, 20·95 per cent.; according to the formula Cd Br + 4 aq it should be 21·17: it fuses easily and crystallizes on cooling. Bromide of cadmium dissolves in hot caustic ammonia, and gives on cooling a granular crystalline powder; by slow cooling the salt is deposited in the form of regular octohedrons. It contains 11·69 per cent. of ammonia, or 1 atom, and is therefore analogous to the chloride.

The anhydrous bromide absorbs a large quantity of ammonia, like the chloride, but the quantity varies between two and three atoms*.

All these compounds are decomposed by water, and oxide of cadmium is separated.

The chloride, bromide and iodide of cadmium form very beautiful double salts with the alkaline chlorides, bromides and iodides.

They may be prepared by dissolving the respective salts in atomic proportions.

Cadmio-chloride of potassium.—From the concentrated solution the salts crystallize in silky needles which contain water. If these crystals be allowed to stand in the solution they gradually disappear, and large crystals are formed in their stead; they have the form of regular rhombohedrons; they contain no water. Their formula is Cd Cl + KCl; the acicular salt contains one atom of water. 100 parts of water at 60° F. dissolve 33·45.

Cadmio-bromide of potassium is precisely similar to the double chloride: it is, however, much more soluble in water. Formula Cd Br + KBr. The acicular salt contains water.

Cadmio-iodide, &c., does not crystallize like the bromide and chloride; the anhydrous salt is Cd I + K I. It is very soluble in water.

Cadmio-chloride of sodium does not crystallize in a regular form, but in verrucose crystals. The formula is Cd Cl + Na Cl + 3 aq. 100 parts of water at 60 dissolve — 71·32.

Cadmio-chloride of ammonium crystallizes like the potassium salt in two forms; the large crystals are anhydrous.

All these salts are somewhat soluble in alcohol and wood-spirit, but not so much so as the simple chloride, iodide and bromide.

The analyses of these, as well as some other salts of cadmium, will be published in a second paper.

* In the last number of the Reports of the Academy of Berlin, I find that Rammelsberg has prepared and analysed the crystallized bromide and its compounds with ammonia. That prepared in the dry way contains, as he says, two atoms of ammonia.

XXI. *Experiments on the Heat disengaged in Combinations.* *By* Thomas Graham, *Esq.*, *F.R.S.*, *&c.*

Read November 1, 1842.

THE observations, of which an account shall be given in the present paper, are exclusively confined to the heat disengaged in combinations formed in the humid way. The heat disengaged in such combinations is in general easily collected and measured, as it is immediately communicated to a mass of fluid, of which the temperature may be observed with accuracy. The elevation of temperature in an experiment may often, however, be greatly affected by incidental circumstances; such as the liquefaction of the product of the combination, arising from its solution in the water, or other menstruum employed; or the hydration of the compound formed, which so generally occurs with a salt formed by uniting an acid and base; and can rarely, therefore, be taken as the expression of the heat disengaged from the combination without considerable correction.

Thus in a few preliminary experiments to ascertain whether, as has been anticipated, different bases of the same class evolve equal quantities of heat on combining with the same acid, it was found that equivalents of oxides of copper and zinc, and the equivalent of magnesia on dissolving in highly diluted sulphuric acid, evolved respectively 4°·20, 5°·18, and 11°·70. But the sulphates formed are all hydrated salts, and a large portion of the heat was found to be due to the combination of this water, namely 3°·49 in the sulphate of copper, 3°·90 in the sulphate of zinc, and 4°·12 in the sulphate of magnesia. Again, the salts are obtained in solution; now the liquefaction or solution of salts is attended with the absorption of a certain quantity of heat or fall of temperature, namely by a fall of 0°·66 in the hydrated sulphate of copper, 0°·93 in the hydrated sulphate of zinc, and 0°·83 in the hydrated sulphate of magnesia. The last quantities being added to the heat first observed in the solution of the oxides, and the preceding quantities being subtracted from the same heat first observed, we obtain as the corrected determinations of the heat evolved from the combination with sulphuric acid of the oxides enumerated (or rather from the substitution of these metallic oxides for the basic water of the sulphate of water), by oxide of copper 1°·37, by oxide of zinc 2°·21, by magnesia 8°·41; quantities which, so far from being equal, are nearly in the ratio of the numbers 2, 3, and 12. It is obvious, therefore, that experiments to determine both the heat absorbed in the solution of salts, and that evolved in their

hydration, must precede inquiries respecting the heat disengaged in the formation of the salts themselves by the combination of their essential constituents, when the salts are formed in the humid way.

The apparatus employed consisted of a delicate thermometer of small bulb, namely, that used in the wet-bulb hygrometer, as prepared by Greiner of Berlin. Every degree was divided into five parts, each part again was divisible by the eye into five parts, so that observations were made to $\frac{1}{25}$th of a degree. The degree is that of Reaumur's scale. After trying glass jars and various other vessels, it was found that nothing answered better than a large platinum crucible, which weighed 1201·9 grains, and was capable of containing 5 ounces of water. The thermometer and crucible, with a hollow cylinder of palladium, weighing 207·6 grains, employed as a stirrer, were all the apparatus necessary. Of the salt or other substance experimented upon, a quantity corresponding with its atomic weight, and representing a single equivalent, was always used; and the quantity of water was constant, namely 1000 grains, and relatively large, so as to render the change of the specific heat of the fluid insensible.

The water, crucible, stirrer and thermometer, being the same in all the experiments, the results are strictly comparable. The numbers express the relative quantities of heat disengaged from atomic equivalents of the bodies.

I. *Hydration of Oil of Vitriol.*

1. H O, S O. The protohydrate of sulphuric acid employed was pure, and of density 1·848. The quantity used of this and other substances was always one-twentieth of the number expressing the equivalent taken in grains; that is 30·68 grains of oil of vitriol, the equivalent of the protohydrate being 613·5. It was weighed in an exceedingly thin and light glass spherule, which was afterwards broken in the water, and the acid diffused through the latter. The greater portion of the heat is disengaged in the first two or three seconds after mixture, or its evolution is almost instantaneous. To avoid the loss of heat by communication to the air, during the short time that must elapse before the thermometer in the liquid becomes stationary, the crucible, water and stirrer were previously cooled down so far below the temperature of the air, as the liquid was expected, from a preliminary experiment, to rise on the addition of the acid. The crucible was also placed within a glass jar containing tow, to impede the passage of heat by conduction. I am indebted for several valuable hints on the mode of conducting

such experiments, to the papers of Dr. Andrews and Professor Hess, who have preceded me in similar investigations.

The rise of temperature in a preliminary experiment, in which the water and crucible were not previously cooled, was 3°·78 R. In two other experiments in which the crucible and water were previously cooled before the addition of the acid, the rise was 3°·88 and 3°·85. The mean of the last results, or 3°·86, may therefore be taken as the heat disengaged in the hydration of an equivalent of the protohydrate of sulphuric acid. No perceptible change of temperature occurred on diluting further with water the products of these experiments.

2. $HO, SO_3 + HO$. This is the crystallizable hydrate of sulphuric acid, of density 1·78. 36·3 grains, the equivalent quantity, were mixed with 1000 grains of water, as in the preceding case. The rise of temperature in three experiments was 2°·40, 2°·36 and 2°·40; of which the mean is 2°·39.

The dilution of this hydrate gives occasion to the disengagement of 1°·47 less heat than the preceding hydrate. It appears, therefore, that in the dilution of the first hydrate or of sulphate of water, 1°·47 is due to the combination of the first atom of water, with which it forms the crystallizable hydrate, and 2°·39 to combination with all the rest, making together 3°·86.

3. $HO, SO_3 + 2HO$. This is the hydrate of sulphuric acid in the formation of which the greatest contraction is observed to occur. With 41·93 grains, or one equivalent, the rise of temperature on dilution was in three experiments conducted as before, 1°·88, 1°·86 and 1°·85, of which the mean is 1°·86. The difference between the heat evolved by the present and the immediately preceding hydrate is 0°·53, which is therefore the heat evolved by the addition of the second atom of water to the sulphate of water. It is scarcely one-third of 1°·47, the quantity evolved by the first atom.

4. $HO, SO_3 + 3HO$. With 47·55 grains, or one equivalent of this hydrate, the rise by dilution was in three experiments 1°·31, 1°·31 and 1°·27, of which the mean is 1°·30. The difference between the heat evolved by this and the preceding hydrate is 0°·56, which is therefore the heat evolved by the addition of the third atom of water to the sulphate of water. Now the second atom evolved 0°·53, so that the second and the third atoms of water appear to evolve sensibly the same quantity of heat. This curious result favours the conclusion, that the second and third atoms of water go together; or that the hydration of the sulphate of water here advances by two atoms at a time, and that no intermediate hydrate exists, in a state of solution at least, between $HO, SO_3 + HO$

and $HO, SO_3 + 3\,HO$. The last may be represented as $HO, SO_3, HO + 2\,HO$.

5. $HO, SO_3 + 4\,HO$. With 53·18 grains, or one equivalent of this hydrate, the rise of temperature on dilution was 1°·05, 1°·07 and 1°·05; mean 1°·06. The difference between this and the preceding hydrate, namely 0°·24, is therefore the heat evolved by the combination of the fourth atom of water with sulphate of water.

6. $HO, SO_3 + 5\,HO$. With 58·8 grains, or one equivalent of this hydrate, the rise of temperature on dilution was 0°·88, 0°·88 and 0°·85; mean 0°·87. The heat from the combination of the fifth atom of water is 0·19. It is not impossible that the heat evolved from the fifth is the same in quantity as that evolved from the fourth atom of water, and that these two atoms go together like the second and third. The present hydrate of sulphate of water corresponds with crystallized sulphate of copper.

7. $HO, SO_3 + 7\,HO$. With 70·05 grains, or one equivalent, the rise was 0°·68, 0°·71 and 0°·65; mean 0°·68. The difference between the effect of this and the preceding hydrate is 0°·19, which is therefore the heat evolved by the combination of the last two atoms of water, namely the sixth and seventh atoms. This hydrate of sulphate of water corresponds with crystallized sulphate of magnesia.

By the continued hydration of the sulphate of water, the quantities of heat evolved are therefore as follows:—

	Heat evolved.	Hydrate formed.
By first atom of water	1°·47 ...	$HO, SO_3 + HO$.
By second and third atoms together .	1°·09 ...	$HO, SO_3 + 3\,HO$.
By fourth and fifth atoms together . .	0°·43 ...	$HO, SO_3 + 5\,HO$.
By sixth and seventh atoms together .	0°·19 ...	$HO, SO_3 + 7\,HO$.
By an additional excess of water . . .	0°·68 ...	$HO, SO_3 + 7\,HO + x\,HO$.

It will be observed that the heat evolved by the first atom is sensibly the same as that evolved by the four following atoms, the quantities being 1°·47 and 1°·52; the difference between these numbers being within the limits of errors of observation. The same conclusion is drawn from his experiments on the hydration of oil of vitriol by Professor Hess. Supposing the whole heat disengaged in the hydration of sulphate of water to be divided into 23 parts, 9 are evolved by the first atom of water, 9 by the next four atoms, 1 by the following two atoms, and 4 by the remaining excess.

Although the experiments detailed above agree with those of M. Hess in bringing out one curious result, they yet differ from them to an extent which it is difficult to account for in other respects. Thus reducing my results to the same

scale as those of M. Hess, the comparison is as follows. In the hydration of the sulphate of water,

	Hess.	Graham.
Heat from the first atom of water . . .	2	2·
... second atom of water . .	1	0·72
... next three atoms of water	1	1·35
... additional excess of water	1	1·18
	5	5·25

8. $HO, SO_3, HO + 10\,HO$. An equivalent quantity of this hydrate, or 92·55 grains, was mixed with 969·3 grains of water, the quantity of the latter being diminished so as to make up 1000 grains with the water already in the acid hydrate. The rise of temperature in two experiments was 0°·37 and 0°·41, of which the mean is 0°·39. This hydrate contains four atoms more of water than the last operated upon, and disengages 0°·29 less heat. The heat, therefore, due to the combination of the additional four atoms of water is 0°·29.

9. $HO, SO_3, HO + 14\,HO$. Of this hydrate the equivalent, or 115·05 grains, was mixed with 915·6 grains of water, and occasioned a rise of temperature in two experiments of 0°·23 and 0°·20, of which the last was believed to be the most trustworthy result. Hence the four atoms of water last added evolve 0°·09, or about one-third of the quantity evolved by the preceding four atoms of water.

10. $HO, SO_3, HO + 24\,HO$. The equivalent of this hydrate, or 171·3 grains, was mixed with 859·4 grains of water, and produced in one experiment a rise of 0°·15. The hydrate was kept for three days before it was diluted in the experiment; for immediately after its preparation the heat which this hydrate yielded on dilution was considerably less than the quantity assigned above to it; indeed not more than 0°·06 in one experiment.

11. $HO, SO_3, HO + 36\,HO$. The equivalent quantity of this diluted acid, or 238·8 grains, was mixed within an hour of its preparation with 792 grains of water; the rise of temperature was 0°·11.

12. $HO, SO_3, HO + 48\,HO$. The equivalent quantity, or 306·3 grains, was mixed about three hours after its preparation with 724·4 grains of water; a rise occurred of 0°·08. The dilution of the same hydrate twenty-four hours after its preparation was attended with a rise of 0°·13.

The last hydrate is oil of vitriol diluted with nine times its weight of water, yet it was still capable of evolving a sensible quantity of heat by further dilution. The term at which the mixture of acid and water ceases to disengage heat

on a further addition of water, was not observed, but the effect was insensible in a mixture formed of one part of the concentrated acid and thirty parts of water.

II. *Hydration of other Magnesian Sulphates.*

The heat produced in the hydration of different anhydrous sulphates, compared with oil of vitriol, appears in the following results; equivalent quantities of the anhydrous salts in the solid state being thrown into the same quantity of water, and the rise of temperature observed after the hydration and complete solution of the salts.

Protosulphate of manganese	3°·22
Sulphate of copper . . .	3°·73
Sulphate of water . . .	3°·86
Sulphate of zinc	4°·17
Sulphate of magnesia . .	4°·33

The most material difference in the circumstances of the experiments is, that while the oil of vitriol was liquid, the salts with which it is compared were necessarily applied in the solid form. The liquefaction of the latter during the experiment, would therefore occasion an absorption of heat of unknown amount, which does not occur in the latter.

1. *Sulphate of Magnesia.*—The same mode of experimenting was followed and apparatus used as in the preceding experiments with oil of vitriol. On dissolving the equivalent quantity, 77·35 grains (one-twentieth of 1547·02), of the crystallized salts in 960·6 grains of water, a fall occurred in three experiments of 0°·96, 0°·90 and 0°89, of which the mean is 0°·92. In these experiments, the water contained in the crystals, which amounts to 39·4 grains, was deducted from the 1000 grains of water usually employed to dissolve the salt; but if this quantity of water is supposed to be added, the mean result would become 0°·88.

The salt was made certainly anhydrous by exposure to an incipient red heat for a considerable time, and the equivalent quantity, 37·98 grains, in the state of a fine powder, was thrown into 1000 grains of water. It did not cake, and was dissolved completely by stirring in about one minute and a half. The rise of temperature in two experiments was 4°·30 and 4°·36, of which the mean is 4°·33. To this must be added the heat lost by the liquefaction and solution of the hydrate formed.

Rise on solution of MgO, SO_3	4°·33
Fall from solution of $MgO, SO_3 + 7\,HO$	0°·92
Whole heat disengaged by MgO, SO_3 .	5°·25

MgO, SO_3, HO. It is not easy to obtain the sulphate of magnesia with exactly one atom of water. The salt first operated upon retained, after being dried by an oil-bath, at 400° to 100 sulphate of magnesia only 14·14 water, instead of 14·81, the single equivalent. The hydrate was therefore $\frac{21}{22}$ HO. The heat evolved by the solution of 43·35 grains, an equivalent quantity of this hydrate in two experiments, was 3°·06 and 3°·9, of which 3°·08 may be taken as the mean.

Another portion of the same sulphate less strongly dried, retained to 100 sulphate of magnesia 15·75 water, which is $1\frac{1}{17}$ HO. The results from the solution of 43·93 grains, the equivalent of this hydrate, were 3°·03, 2°·98 and 2°·93, of which the mean is 2°·98. The mean of the two sets of experiments, or 3°·03, probably does not differ far from the truth.

Rise on solution of MgO, SO_3, HO . .	3°·03
Fall on solution of $MgO, SO_3, + 7HO$.	0°·92
Whole heat disengaged by MgO, SO_3, HO	3°·95

The anhydrous salt disengaged 5°·25, while the protohydrate disengages 3°·95; the difference, or 1°·30, is therefore the heat disengaged by the combination of the first atom of water with sulphate of magnesia. It thus appears that of the whole heat evolved in the complete hydration of sulphate of magnesia, as nearly as possible one-fourth is due to the combination of the first atom of water, one-fourth of 5°·25 being 1°·31.

2. *Sulphate of Zinc.*—The equivalent quantity of the crystallized salt, 89·59 grains, contains 39·38 water, and was therefore dissolved in 960·6 water. The fall of temperature in two experiments was 1°·01 and 0°·98, of which the mean is 1°·00. This sensibly exceeds the cold produced by the solution of crystallized sulphate of magnesia, which is 0°·92. The difference has a real foundation, and is not the consequence of errors in experiment; for in two other sets of observations on the same salts made in glass, and which may be compared with each other, although not with the preceding experiments, the results were for sulphate of magnesia 0°·85, 0°·80 and 0°·83, of which the mean is 0°·83; for sulphate of zinc 0°·97, 0°·91, 0°·92, of which the mean is 0°93: greater cold occasioned by the solution of sulphate of zinc than of sulphate of magnesia, by the first experiments 0°·08, by the last experiments 0°·10.

Of sulphate of zinc, carefully dried and made perfectly anhydrous, the equivalent quantity, 50·22 grains, was dissolved in 1000 grains of water, with the exception of a mere trace of flaky matter. The rise in one experiment was 4°·20; in another 4°·15; mean 4°·17. The results then are,—

Rise on solution of Zn O, $S O_3$	4°·17
Fall on solution of Zn O, $S O_3$ + 7 H O .	1°·00
Whole heat disengaged by Zn O, $S O_3$ . .	5 ·17

There is the same difficulty in obtaining the protohydrate of sulphate of zinc exactly definite, as the corresponding hydrate of sulphate of magnesia. The hydrate operated upon contained to 100 sulphate of zinc 11·99 water, instead of 11·207, which is a single equivalent. The equivalent quantity, 56·21 grains, was dissolved in 1000 grains of water, and occasioned a rise of temperature in two experiments of 2°·34 and 2°·33. As the rise for the anhydrous salt was 4°·17, the deficiency from the hydrate, 4·17 − 2·34 = 1°·83, is due to the quantity of water already combined in the salt of the experiment. But this deficiency cannot be entirely ascribed to a single atom of water, as the combined water exceeded that proportion as 11·99 to 11·21. It is difficult to find proper elements for the necessary correction, but we may probably reduce the amount of deficient heat to 1°·71, that is, as 11·99 to 11·21, without any considerable error. Hence

Rise on solution of Zn O, $S O_3$, H O . .	2°·45
Fall on solution of Zn O, $S O_3$ + 7 H O .	1°·00
Whole heat disengaged by Zn O, $S O_3$, H O	3°·45

The difference between the heat disengaged by the protohydrate and the anhydrous salt, or the heat due to the combination of the first atom of water, namely 1°·71, is almost exactly one-third of the whole heat disengaged in the hydration of sulphate of zinc; one-third of 5°·17 being 1°·72. The quantities of heat disengaged by sulphate of zinc in the two conditions specified, are therefore as 4 to 6.

3. *Sulphate of Copper.*—The equivalent quantity of the ordinary crystallized salt, containing 5 H O, namely 77·97 grains, was dissolved in 1000 grains of water, with a fall of temperature in three experiments of 0°·67, 0°·65 and 0°·68, of which the mean is 0°·67. This and other more sparingly soluble salts were pounded fine and sifted; the solution took place with stirring within one minute.

Of the anhydrous salt, 49·84 grains, the equivalent quantity, were dissolved in 1000 grains of water, with a rise in two experiments of 3°·72 and 3°·74. Hence the results for the anhydrous salt are,—

Rise on solution of Cu O, $S O_3$	3°·73
Fall on solution of Cu O, $S O_3$ + 5 H O .	0°·67
Whole heat disengaged by Cu O, $S O_3$ . .	4°·40

The protohydrate was prepared by drying the crystallized

salt by a nitre-bath; it retained to 100 sulphate of copper 11·83 water, instead of 11·29 water, the single equivalent. The equivalent quantity, 55·72 grains, was dissolved in 1000 grains of water, with a rise in two experiments of 2°·15 and 2°·13. The result is 3·73 − 2·14 = 1°·59 for the combined water. This hydrate contained $1\frac{1}{22}$ H O.

After being dried still further on an oil-bath at 370°, it consisted of 100 sulphate of copper and 11·44 water, or was $1\frac{1}{73}$ H O; the salt was now almost white, the green tint being barely perceptible. The equivalent quantity of the last salt, 55·54 grains, was dissolved in 1000 grains of water, but somewhat more slowly and with greater difficulty than the preceding salt. The heat evolved in two experiments was 2°·09 and 2°·07, which instead of exceeding falls short of the preceding results. The deficiency of heat in the last experiments is remarkable, and is in some measure, but I believe not fully, accounted for by the slowness of the solution. Giving a preference to the first results, and deducting $\frac{1}{22}$nd part for the excess of water above one atom already combined with the salt, there remains 1°·47 for the heat due to the combination of the first atom of water. The result for the protohydrate is,—

Rise on solution of Cu O, $S O_3$, H O . .	2°·26
Fall on solution of Cu O, $S O_3$ + 5 H O .	0°·67
Whole heat disengaged by Cu O, $S O_3$, H O	2°·93

One-third of 4°·40, the whole heat evolved in the hydration of sulphate of copper, is 1°·466, which is as nearly as possible the result obtained above for the first atom of water. The ratio is the same as in the sulphate of zinc, while in the hydration of the sulphate of magnesia the heat evolved by the first atom of water was one-fourth of that evolved by the whole. It may be inferred from the experiments on oil of vitriol, that it approaches more closely to the former salts than to sulphate of magnesia in this character, although a rigid comparison cannot be made, as we are unacquainted with the fully hydrated sulphate of water in a crystalline form, and cannot therefore estimate its heat of liquefaction.

4. *Protosulphate of Iron.*—Of the crystallized salt containing seven atoms of water, the equivalent quantity, 86·39 grains, dissolved in 1000 grains of water in two experiments with a fall of 1° and 1°·04. Allowing for the 39·38 grains of water introduced by the salt in addition to the thousand grains employed, these results become 1°·04 and 1°·08, of which the mean is 1°·06.

Fall on the solution of Fe O, $S O_3$ + 7 H O...1°·06.

The protohydrate of sulphate of iron, formed by drying

the crystallized salt in air at a temperature approaching 400°, was found to be nearly insoluble in cold water. The anhydrous sulphate was more soluble, but not sufficiently so for the determination of its thermal relations.

5. *Protosulphate of Manganese.*—The crystallized salt employed contained five atoms of water. The equivalent quantity, 75·47 grains, of the crystallized salt was dissolved in 972 grains of water at 59° Fahr., with a fall of temperature in two experiments of 0°·11 and 0°·13 R., of which the mean is 0°·12.

Of the same salt made anhydrous by heat, the equivalent quantity, 47·35 grains, was dissolved in 1000 grains of water at 60° Fahr., with a rise in two experiments of 3°·20 and 3°·24 R.; mean rise 3°·22.

Rise on solution of Mn O, $S O_3$	3°·22
Fall on solution of Mn O, $S O_3 + 5$ H O .	0°·12
Whole heat disengaged by Mn O, $S O_3$.	3°.34

The crystallized salt being well dried at a temperature not exceeding 400° Fahr., was found to retain a quantity of water in combination, which slightly exceeded a single equivalent, namely in the proportion of 5·82 grains to 5·62 grains, in 52·97 grains of the hydrated salt. The heat evolved in the solution of the equivalent quantity, 52·97 grains, of this protohydrate by 1000 grains of water was in two experiments 1°·80 and 1°·78, of which the mean is 1°·79.

Rise on solution of Mn O, $S O_3$, H O . .	1°·79
Fall on solution of Mn O, $S O_3 + 5$ H O .	0°·12
	1°·91

It follows that the heat evolved by the combination of the first atom of water with sulphate of manganese is 3°·34 − 1°·91 = 1°·43. This result approaches to 1°·47, the heat evolved by the combination of the first atom of water with sulphate of copper. The small depression of temperature produced by the solution of crystallized protosulphate of manganese is remarkable, and distinguishes this salt from the other magnesian sulphates. This salt alone of the class forms a thick solution, when highly concentrated, and crystallizes with difficulty. It was also observed that the protohydrate of sulphate of manganese does not dissolve easily in cold water; the quantity of the protohydrate employed in the experiments narrated above requiring to be agitated with the water for two and a half minutes, before the liquid ceased to be turbid and the salt was entirely dissolved. The anhydrous sulphate of manganese was dissolved quickly and with ease.

III. *Sulphates and Chromates of the Potash family.*

1. *Sulphate of Potash.*—Good crystals of this salt were reduced to powder and sifted. The solution of the equivalent quantity, 54·55 grains, in 1000 grains of water, which took place in thirty seconds, was attended by a fall of temperature in two experiments of 1°·50 and 1°·52, of which the mean is 1°·51.

Fall on solution of K O, SO_3 . . . 1°·51.

The same quantity of sulphate of potash was dissolved in a mixture of 300 water-grain measures of dilute sulphuric acid of density 1·1 mixed with 700 grains of water. The dry acid in the mixture amounted to 36 grains; a single equivalent is represented by 25 grains. The solution was quite as rapid, or more so, than in pure water; the fall of temperature 2°·04; the difference of 0°·53 is probably connected with the formation of bisulphate of potash.

2. *Chromate of Potash.*—The solution of the equivalent quantity, 62·09 grains, of this salt in 1000 grains of water, was attended with a fall of 1°·18 in water.

Fall on solution of K O, CrO_3 . . . 1°·18

When dissolved in an equal quantity of the same dilute sulphuric acid as was used with sulphate of potash, the solution became red from the formation of bichromate, and only a very slight change of temperature occurred, namely a fall of 0°·08.

3. *Bichromate of Potash.*—The fused salt was used, as it is easily reduced to a fine powder, and half the equivalent quantity used, as the whole equivalent is not dissolved by 1000 grains of water at 57° Fahr., the temperature of the experiments. The solution of 47·34 grains, half the equivalent quantity, was attended with the same fall of 1°·98 in two experiments. No sensible change of temperature occurred on diluting this solution. In the dilute sulphuric acid used with the two preceding salts, the fall on the solution of half an equivalent of bichromate of potash was 2°·00, or sensibly the same as in pure water. The fall of temperature for a whole equivalent of bichromate of potash will therefore be 3°·96.

Fall on solution of K O, 2 CrO_3 . . 3°·96

The heat of liquefaction of bichromate of potash is therefore very considerable. It appears to be the same in quantity as that of *nitrate of potash*. The equivalent quantity of the latter salt, 63·25 grains, was dissolved in 1000 grains of water, with a fall of 3°·86. The temperature of this solution was further reduced 0°·10, by dilution with another 1000 grains

of water; so that by the solution of an equivalent quantity of this salt in the same proportion of water as was employed for the solution of an equivalent of bichromate of potash, a fall of temperature of 3°·96 is produced. In a second experiment the whole fall of temperature on the solution of an equivalent of nitrate of potash was 3°·95.

Fall on solution of K O, $N O_5$ . . . . . 3°·96

It is possible that this coincidence is not accidental, but depends on a thermal equivalency of $N O_5$ and $Cr_2 O_6$, the acids united with potash in these two salts. If the single equivalent of nitrogen in nitric acid be divided by three, or considered three atoms instead of one, as has been inferred on other grounds, then the acid constituents of both salts will contain the same number of atoms, namely eight; and the bichromate of potash, which has hitherto appeared so anomalous among salts, be assimilated to the nitrate of potash.

4. *Terchromate of Potash.*—Of this salt 63·63 grains, or one-half of the equivalent quantity, were dissolved easily and entirely by 1000 grains of water, with a fall of 1°·63. But the terchromate of potash changes colour when thrown into water from decomposition, being resolved in a great measure into bichromate of potash and chromic acid, both of which are soon dissolved, the last more rapidly than the first.

Half an equivalent of this salt was dissolved, with a fall of 1°·28, in 1000 water-grain measures of dilute nitric acid, of specific gravity 1·1453. But in this menstruum also, the terchromate appeared to be decomposed with separation of chromic acid, although to a much less extent than in the preceding experiment. In a liquid, however, already charged with the salt, like the last, an additional quantity may be dissolved without further decomposition. Half an equivalent of the salt was dissolved in that liquid with a fall of 1°·14, which is a fall of 2°·28 for a whole equivalent of the salt. The capacity for heat of the solution in question does not (I believe) differ materially from that of 1000 grains of water.

Fall from solution of K O, 3 $Cr O_3$ . . . 2°·28

Half an equivalent of the crystallized *biphosphate of potash*, or 42·68 grains, was dissolved in 1000 grains of water, with a fall of 1°·12, which gives 2°·24 for the whole equivalent.

Fall from solution of 2 H O . K O, $P O_5$. 2°·24

A corresponding proportion of the crystallized *binarseniate of potash*, or 56·38 grains, were dissolved by 1000 grains of water, with a fall in one experiment of 1°·13, and in another of 1°·18. In a third experiment the solution of a whole equi-

valent of this salt, or 112·75 grains, was attended by a fall of temperature of 2°·15. A greater discrepancy is observable in the results obtained from this than from most other salts, which appeared to arise from the full depression of temperature not occurring at the moment of solution, but a small portion of it being produced in a gradual manner for three or four minutes after the solution. The mean of the three observations gives 2°·26 for the equivalent quantity of the salt.

Fall from solution of 2 H O . K O, As O_5 . 2°·26

The thermal properties of these two salts are interesting in relation to the terchromate of potash. The latter salt contains 14 atoms, which is also the number of atoms in both biphosphate and binarseniate of potash, if the equivalents of phosphorus and arsenic be supposed, like that of nitrogen, to represent three atoms.

Potash being common to the terchromate and biphosphate of potash, there remain, on subtracting that constituent from both salts, three equivalents of chromic acid equivalent in some sense to one equivalent of phosphoric acid together with two equivalents of water. This statement respecting phosphoric acid, recalls the view which has lately been proposed by M. Wurtz of the constitution of the hypophosphites, in which the two atoms of water which they all contain are supposed not to be basic, but to form part of the acid; a neutral hypophosphite being represented by $RO + PO,H_2O_2$, or rather by $RO + PO_3H_2$. For we are here representing biphosphate of potash as $KO + PO_7H_3$, corresponding with the terchromate of potash $KO + Cr_3O_9$, in which P is equivalent to Cr_3, and $O_7 + H_2$ to O_9. The two atoms of water, however, may be replaced by a strong base in a biphosphate, but not in a hypophosphite. The relations of these salts show a progressive and imperceptible passage of the basic elements of a salt into constituents of its acid, and the existence of intermediate conditions of the elements in question, which we may well conceive although our chemical formulæ fail to enable us to denote them; these formulæ being adapted only for the expression of the extreme conditions.

Of anhydrous *chromic acid* an equivalent, 32·59 grains, was dissolved by 1000 grains of water with a rise of 0°·51. A second equivalent, dissolved in the previous solution, produced a rise of only 0°·38. The relations of this acid to water are therefore very different from those of sulphuric acid.

5. *Sulphate of Soda.*—In removing the hygrometric water which the crystals of this salt generally contain in large quantity, by pressure in blotting-paper, the salt is apt to lose a

little of its combined water. The crystallized salt contained as determined by analysis, to 100 sulphate of soda, 121·5 water, instead of 126·1 water, which are ten equivalents. The equivalent quantity of the fully hydrated salt is 100·85 grains, but of the salt under examination only 98·79 grains. The last quantity, which contains 54·2 grains of water, was dissolved in 946 grains of water in half a minute, with a fall of 4°·43. The fall is almost entirely due, as will immediately appear, to the liquefaction of the combined water of the salt, of which the quantity liquefied in the experiment was 54·2 grains instead of 56·2, the ten equivalents. The fall of 4°·43 increased in the proportion of 54·2 to 56·2, becomes 4°·59.

Fall on solution of Na O, S O_3 + 10 H O . . 4°·59.

The same quantity of the salt was dissolved in the diluted sulphuric acid of the experiments with the previous salts, with a fall of 5°·00; which, corrected in the same manner as the last result, gives a fall of 5°·19 for the equivalent of the salt. Hence the fall on the solution of the sulphate of soda in dilute sulphuric acid is 0°·60 greater than in pure water; a circumstance connected probably with the formation of bisulphate of soda.

Sulphate of soda was made anhydrous by a strong heat, without being fused. The solution of the anhydrous salt is difficult, owing to the instantaneous formation of a hard coherent mass when the salt is thrown into water, which it requires two or three minutes to break up and dissolve. Very little change of temperature occurs. A rise took place in one experiment of 0°·10. In another experiment, in which the salt was added in a gradual manner with constant stirring, there was less caking, and the solution more rapid, although it still required two minutes. A rise occurred of 0°·18. The last experiment is most to be depended upon. The results for the sulphate of soda will therefore be,—

Rise on solution of Na O, S O_3	0°·18
Fall on solution of Na O, S O_3 + 10 H O .	4°·59
Whole heat disengaged by Na O, S O_3 . .	4 ·77

The last number represents the heat evolved in the formation of a solid hydrate of sulphate of soda containing ten atoms of water; it is remarkable how little it exceeds the heat disengaged in the crystallization of the same salt, or the fall observed on the solution of the crystallized salt. It appears as if water abandoned little more than its heat of fluidity on combining with dry sulphate of soda to form a solid hydrate.

Sulphate of soda, which had been allowed to effloresce in

dry air between 50° and 55° Fahr. for a week, consisted of dry salt 100 and water 0·46. The equivalent quantity of this salt, which is so nearly anhydrous, or 44·81 grains, was dissolved in 1000 grains of water with a very slight change of temperature, namely a rise of 0°·05.

6. *Sulphate of Ammonia.*—Of the hydrated salt crystallized by spontaneous evaporation in air, which contains one atom of water of crystallization, the equivalent quantity, 47·03 grains, was dissolved in 1000 grains of water with a fall of temperature in three experiments of 0°·65, 0°·64 and 0°·61, of which the mean is 0°·63.

Fall on solution of $N H_4 O, S O_3 + H O$. 0°·63.

The salt was obtained anhydrous by drying at 248° Fahr.; it was granular and crystalline, and neutral to test paper. The equivalent quantity, 41·41, produced a fall in three experiments of 0°·51, 0°·53 and 0°·49; of which the mean is 0°·51.

Fall on solution of $N H_4 O, S O_3$ . . . 0°·51.

A sensible but very small reduction of temperature, not exceeding 0°·02, occurred on mixing the solution of sulphate of ammonia with an equal bulk of water at the same temperature.

Dissolved in the diluted acid, consisting of a mixture of 300 water-grain measures of sulphuric acid of density 1·1 and 700 grains of water, the equivalent, 41·41 grains, of the anhydrous salt produced a fall of temperature in two experiments of 1°·17 and 1°·14; of which the mean is 1°·16. Hence the fall is greater on the solution of the sulphate of ammonia in dilute sulphuric acid than in water, by 0°·65. The fall of sulphate of soda was also greater by nearly the same amount, 0°·60, and of sulphate of potash by 0°·53, when these salts were dissolved in the same dilute acid instead of water.

IV. *Double Sulphates.*

1. *Bisulphate of Potash.*—Of the usual double sulphate of water and potash crystallized in rhombohedral crystals, an equivalent quantity, 85·23 grains, was dissolved in 1000 grains of water, with a fall in two experiments of 1°·96 and 1°·95. The same salt was fused by heat and pounded; it dissolved afterwards with a fall of 1°·94 and 1°·90 in two experiments. The cold upon solution of this salt appears to be the same before and after fusion. The result is,—

Fall on solution of $H O, S O_3 + K O, S O_3$. 1°·95.

I was anxious to compare with this salt the anhydrous bi-

sulphate of potash of M. Jacquelin, which is described as being capable of dissolving in water without decomposition. One equivalent of sulphate of potash was accordingly dissolved in two equivalents of oil of vitriol, with the aid of heat, and an abundant crop was obtained on cooling of a salt in small silky crystals. As these appeared to be the salt in question, an equivalent quantity, or 79·60 grains, was dissolved, and a fall observed of 1°·90. The result not differing from that of the former salt, the preparation of the anhydrous salt was repeated. The spongy mass of thin prismatic crystals obtained in a second experiment was pressed, dissolved again in water, crystallized and pressed again. The salt was still in minute prisms. The solution of 39·8 grains, half the equivalent quantity, was attended with a fall in two experiments of 0°·91 and 0°·95; or, for a whole equivalent, 1°·86. Of the same salt, before the second solution, half an equivalent produced a fall of temperature of 0°·96; or, for the whole equivalent, 1°·92. These results are identical with those formerly obtained with the hydrated bisulphate, if allowance be made for the smaller quantity of the salt employed, a circumstance which excited a doubt as to the composition of the prismatic salt. The product of the second crystallization was accordingly analysed; 19·30 grains of it gave 32·34 grains of sulphate of barytes, equivalent to 11·12 sulphuric acid, or 57·59 per cent.; 22·53 grains of the crystals lost no weight at 150°, but lost 0·24 water, or 1·02 per cent., by cautious fusion. The proportion of acid in the salt is greatly under that of an anhydrous bisulphate, namely 62·98 per cent., while it approaches sufficiently near that of the hydrated bisulphate, 58·74 per cent. The process of M. Jacquelin has not therefore given an anhydrous bisulphate of potash in my hands, and none of my experiments favours the existence of such a salt; the silky prismatic crystals which I obtained being nothing more than an unusual form of the sulphate of water and potash.

2. *Bisulphate of Soda.*—An equivalent quantity, 75·27 grains, of one and the same specimen of this salt, dissolved in three experiments with a fall of 0°·40, 0°·28 and 0°·17. It did not dissolve so easily as the bisulphate of potash, possibly from partial decomposition and formation of a portion of neutral sulphate of soda. The same supposition will explain the want of agreement among the results. Taking the mean of the results,—

Fall on solution of $HO, SO_3 + NaO, SO_3$. 0°·28.

The fall of temperature observed on dissolving bisulphate

of potash in water approaches that observed on dissolving the neutral sulphate of potash in dilute sulphuric acid, the first being 1°·95 and the second 2°·04. But it is doubtful if the fall in the second case can be ascribed simply to the immediate formation and solution of bisulphate of potash, when the sulphate of potash and dilute sulphuric acid are mixed and dissolved together. In the formation of bisulphate of potash we have both the substitution of sulphate of potash for the second atom of water of the sulphate of water, and the throwing off of all the remaining water combined with the sulphate of water in hydrated sulphuric acid, bisulphate of potash containing no water of crystallization. Now as a great deal of heat was disengaged by this additional water on originally combining with the sulphate of water, we should expect heat again to be assumed by that water on becoming free, or cold to be produced.

3. *Sulphate of Magnesia and Potash.*—An equivalent quantity of the crystallized salt, namely 126·28 grains, containing 33·75 grains of water of crystallization, was dissolved in 976·2 grains of water at 52° Fahr., with nearly two minutes' stirring; a fall of temperature was observed of 2°·30 R. The experiment was repeated with the same result. But a slow rise of temperature was afterwards observed to occur in the solution, independent of any external influence, which in the course of four minutes amounted to 0°·20 R. This is not the only salt in which the fall of temperature on solution is immediately followed by a slight but sensible rise.

This salt was made anhydrous by a low red heat to which it was exposed for upwards of two hours, but was not fused. When the salt was thrown into water after this ignition, it gave a liquor which remained white and milky for two or three minutes, but the salt finally dissolved without residue. The rise of temperature on the solution of a whole equivalent of the anhydrous salt, or 92·53 grains, was 1°·57; on solution of one-half of an equivalent, or 46·2 grains, 0°·80; which gives 1°·60 for the whole equivalent.

Rise on solution of $MgO, SO_3 + KO, SO_3$ . . .	1°·60
Fall on solution of $MgO, SO_3 + KO, SO_3 + 6HO$	2°·30
Whole heat disengaged by $MgO, SO_3 + KO, SO_3$	3°·90

The crystallized sulphate of magnesia and potash, dried by a nitre-bath, was found to retain 18·32 water to 100 anhydrous salt. Now 18·24 water represents 3 H O; the crystallized salt has consequently lost one-half of its water, retaining only three atoms. Of this salt, an equivalent quantity, or

109·4 grains, were dissolved in 1000 grains of water, with a fall in three experiments of 1°·35, 1°·30 and 1°·35, of which the mean is 1°·33.

Fall on solution of $MgO, SO_3 + KO, SO_3 + 3HO$ 1°·33.

The fall on the solution of this hydrate is less than on the solution of the former, by the heat disengaged in the combination of the salt with the deficient three atoms of water. The heat disengaged by the union of the salt with the first three atoms of water comes therefore to be 2°·93, and with the second three atoms of water 0°·97, making together 3°·90. Hence as nearly as possible three times as much heat are disengaged by the first three atoms of water as by the last three atoms.

4. *Sulphate of Magnesia and Ammonia.*—The solution of an equivalent quantity, 113·13 grains, of the crystallized salt in 1000 grains of water was attended by a fall of temperature, in two experiments, of 2°·20 and 2°·15, of which the mean is 2°·17. If dissolved in 976·2 grains of water, like the potash salt, the fall would have been about $\frac{1}{30}$th more, or 2°·24.

Fall on solution of $MgO, SO_3 + NH_4O, SO_3 + 6HO$ 2°·24.

The fall on the solution of the corresponding potash salt was 2°·30.

5. *Protosulphate of Iron and Ammonia.*—The solution of 122·17 grains, the equivalent quantity of the crystallized salt in 1000 grains of water, was attended with the same fall of 2°·20 in two experiments. But this determination should be increased by $\frac{1}{30}$th, like the last; the fall then becomes 2°·27.

Fall on solution of $FeO, SO_3 + KO, SO_3 + 6HO$. 2°·27.

6. *Sulphate of Manganese and Ammonia.*—In two experiments 61·20 grains of the crystallized salt, being one half of the equivalent quantity, were dissolved in 983 grains of water with a fall of 1°·11 and 1°·13; or 2°·24 for a whole equivalent.

Fall on solution of $MnO, SO_3 + NH_4O, SO_3 + 6HO$. 2°·24.

It thus appears that the heat of liquefaction of the four crystallized double salts, sulphate of magnesia and potash, sulphate of magnesia and ammonia, sulphate of iron and potash, and sulphate of manganese and ammonia, is sensibly the same.

7. *Sulphate of Zinc and Potash.*—The fall on the solution of half an equivalent, 69·26 grains, of the crystallized salt in 1000 grains of water, was in three experiments 1°·33, 1°·27 and 1°·30, of which the mean is 1°·30. The fall for a whole equivalent, 138·52 grains, is therefore 2°·60.

This salt was made anhydrous by a heat little short of redness, without being fused. Half an equivalent, 52·39 grains,

was dissolved in 1000 grains of water with a rise of temperature of 0°·83 and 0°·87 in two experiments, of which the mean is 0°·85. The rise for a whole equivalent, 104·77 grains of the salt, is therefore 1°·70.

Rise on solution of Zn O, SO_3 + K O, SO_3 . . .	1°·70
Fall on solution of Zn O, SO_3 + K O, SO_3 + 6 H O .	2°·60
Whole heat disengaged in the hydration of Zn O, SO_3 + K O, SO_3	4°·30

8. *Sulphate of Copper and Ammonia.*—Of the crystallized salt, 62·45 grains, or one half of the equivalent quantity, were dissolved in 983 grains of water with a fall of temperature of 1°·33 and 1°·28 in two experiments; giving 2°·63 for the whole equivalent.

Fall on solution of Cu O, SO_3 + NH_4O, SO_3 + 6 H O . 2°·63.

The fall on the solution of the two immediately preceding salts is therefore sensibly the same.

9. *Protosulphate of Iron and Potash.*—Of this salt in small but well-defined crystals, 67·66 grains, one half of the equivalent quantity, were dissolved in 983 grains of water with a fall, in two experiments, of 1°·25 and 1°·22; or for the whole equivalent 2°·47.

Fall on solution of Mn O, SO_3 + K O, SO_3 + 6 H O . 2°·47.

10. *Sulphate of Zinc and Ammonia.*—Of the crystallized salt half an equivalent, 62·64 grains, was dissolved in 983 grains of water with a fall of 1°·37 and 1°·36.

Fall on solution of Zn O, SO_3 + K O, SO_3 + 6 H O . . 2°·73.

11. *Sulphate of Copper and Potash.*—The solution of half an equivalent of the crystallized salt, 69·07 grains, in 1000 grains of water, was attended with a fall in two experiments of 1°·54 and 1°·50; or for the whole equivalent of the salt, 138·14 grains; the fall is 3°·08 and 3°·00, of which the mean is 3°·04.

The crystallized salt was made anhydrous by a heat short of redness, which had the effect of causing it to frit but did not fuse it. The solution of 52·2 grains, half an equivalent, in 1000 grains of water, was attended by a fall in two experiments of 1°·01 and 0°·96; or for a whole equivalent, 2°·02 and 1°·92, of which the mean is 1°·97.

Rise on solution of Cu O, SO_3 + K O, SO_3 . . .	1°·97
Fall on solution of Cu O, SO_3 + K O, SO_3 + 6 H O .	3°·04
Whole heat disengaged in hydration of Cu O, SO_3 + K O, SO_3	5°·01

The fall on the solution of the preceding crystallized double salt is 3°·04, while the fall on the solution of its constituents dissolved separately is 1°·51 for the sulphate of potash, and

0°·67 for the hydrated sulphate of copper, making together 2°·18, which is less by 0°·86 than the former. The fall on the solution of the crystallized double sulphate of zinc and potash approaches more closely to the united falls of its constituents dissolved separately, the former being 2°·60 and the latter 1° + 1°·51 = 2°·51. The fall on the solution of the crystallized double sulphate of magnesia and potash is 2°·30; the united falls of its constituent salts 0°·92 + 1°·51 = 2°·43. No perceptible change of temperature was observed when the solutions of a pair of these salts are mixed to form the double salt; which is in accordance with the conclusion of Dr. Andrews, that no heat is evolved in the combination of salts.

I have not, however, succeeded in obtaining any direct proof of the formation of the double sulphates on mixture. To a solution of 77·97 grains, or one equivalent, of crystallized sulphate of copper in 1000 grains of water, 41·41 grains, one equivalent, of sulphate of ammonia dried at 234° were added and dissolved. The fall on the solution of the last salt was 0°·56, or the same as when the salt is dissolved in pure water. No change took place in the colour of the solution of the copper salt. The last salt was selected for this experiment because it appears more disposed to form double salts than even the sulphate of potash.

In certain cases, a double salt is formed on using a bisulphate, while it is not with the neutral sulphate; as in the formation of sulphate of zinc and soda, from sulphate of zinc and bisulphate of soda, but not from sulphate of zinc and neutral sulphate of soda. To a solution of 85·23 grains, or the equivalent, of crystallized bisulphate of potash in 1000 grains of water, 89·59 grains, or the equivalent, of crystallized sulphate of zinc were added and dissolved, with a fall of 1°·00, or the same as in pure water. To a similar solution of bisulphate of potash, 77·35 grains, or one equivalent, of crystallized sulphate of magnesia were added and dissolved, with a fall of 0°·86; the same fall also as on the solution of the latter salt in pure water. Yet the double salts crystallized out readily from both of these solutions.

I have formerly represented the anhydrous sulphate of magnesia and potash as corresponding with the protohydrated sulphate of magnesia. Now both these salts assume six atoms of water, and the heat then disengaged by the two salts is nearly the same:—

	Heat of hydration.
$Mg\,O, S\,O_3 + K\,O, S\,O_3$	3°·90
$Mg\,O, S\,O_3 + H\,O$	3°·95

When the corresponding salts of zinc are compared, the same equality is not observed, but other relations appear.

	Heat of hydration.
$ZnO, SO_3 + KO, SO_3$	4°·30
$ZnO, SO_3 + HO$	3°·45
ZnO, SO_3	5°·17

These quantities of heat and the quantity disengaged by the anhydrous sulphate of zinc, have a remarkable relation among themselves; if they be all divided by 0°·86, we have

	Ratios of heat of hydration.
$ZnO, SO_3 + HO$	4·01
$ZnO, SO_3 + KO, SO_3$	5
ZnO, SO_3	6·01

The quantity of heat disengaged by the first atom of water on uniting with sulphate of zinc is 1°·71. If it had been only half that quantity, or 0°·86, and had the deficient 0°·86 been evolved by the combination of the six following atoms, in addition to the heat they actually evolve, then the heat disengaged by the six atoms of water which unite with protohydrated sulphate of zinc, and by the double sulphate of zinc and potash, would be the same in both salts, as it is the same in the two corresponding salts of magnesia.

The heat evolved by the corresponding copper salts with their ratios, is as follows:—

	Heat of hydration.	Ratios.
$CuO, SO_3 + HO$ . . .	2°·93	4°
CuO, SO_3	4°·40	6°
$CuO, SO_3 + KO, SO_3$.	5°·01	6°·86

It is to be observed, however, that while the protohydrate of sulphate of copper combines with only four atoms of water, the sulphate of copper and potash combines with six atoms; the usual comparison cannot therefore be made between these two salts.

The principal numerical results of the paper are exhibited in the following tables:—

1. Heat absorbed by equivalent quantities of crystallized salts on dissolving in water.

Sulphate of magnesia	7 HO	0°·92
Sulphate of zinc	...	1°·00
Protosulphate of iron	...	1°·06
Sulphate of copper	5 HO	0°·67
Sulphate of manganese	...	0°·12
Sulphate of magnesia and potash .	6 HO	2°·30
Sulphate of magnesia and ammonia .	...	2°·24
Sulphate of manganese and ammonia	...	2°·24
Sulphate of iron and ammonia . .	...	2°·27
Sulphate of iron and potash . . .	...	2°·47

Sulphate of zinc and potash . . .	6 H O	2°·60
Sulphate of copper and ammonia .	...	2°·63
Sulphate of zinc and ammonia . .	...	2°·73
Sulphate of copper and potash . .	...	3°·04
Sulphate of soda	10 H O	4°·59
Sulphate of potash	anhydrous	1°·51
Sulphate of ammonia	...	0°·51
Chromate of potash	...	1°·18
Bichromate of potash	...	3°·96
Nitrate of potash	...	3°·96
Terchromate of potash	...	2°·28
Biphosphate of potash	2 H O	2°·24
Binarseniate of potash	...	2°·26
Sulphate of water and potash . . .	anhydrous	1°·95

2. Heat disengaged in the complete hydration of anhydrous salts.

Sulphate of magnesia	5°·25
Sulphate of zinc	5°·17
Sulphate of copper	4°·40
Sulphate of manganese	3°·34
Sulphate of magnesia and potash .	3°·90
Sulphate of zinc and potash . .	4°·30
Sulphate of copper and potash .	5°·01

3. Heat disengaged by the combination of the first atom of water in the magnesian sulphates.

Sulphate of water	1°·47
Sulphate of copper	1°·47
Sulphate of manganese	1°·43
Sulphate of magnesia	1°·30
Sulphate of zinc	1°·71

Simple relations are observed between the quantities of heat disengaged by the sulphates of magnesia and zinc, which appear to belong to one class, while the sulphates of water, copper and manganese belong to another class.

XXII. *On Pyrogallic Acid, and some Astringent Substances which yield it.* By Dr. John Stenhouse.

Read November 1, 1842.

THE usual method of procuring pyrogallic acid is by cautiously distilling either gallic or tannic acids. The pyrogallic acid is obtained partly as a crystalline sublimate and partly dissolved in the empyreumatic liquor which passes into the receiver. Pyrogallic acid thus procured is very seldom free from empyreumatic oil, from which it can only be puri-

fied by repeated distillations, in each of which much acid is unavoidably lost. The usual method, therefore, of procuring pyrogallic acid by distillation is troublesome and unproductive. The process which I have found most advantageous for preparing it in quantity, is the following:—

Finely pounded gall-nuts are to be treated with successive portions of cold water till they are exhausted. These extracts are then to be evaporated and strongly dried, till all their hygrometric water is driven off. In this state they form a spongy deliquescent mass, in taste and colour very much resembling catechu. Instead of distilling this dried extract in a retort, it is much better to employ Dr. Mohr's apparatus for subliming benzoic acid. It consists of a cast iron pan from three to four inches deep, and from eighteen inches to two feet wide. The dried extract is coarsely pounded and spread equally over its bottom to the depth of about half an inch. The top of the pan is then covered with a diaphragm of bibulous paper, fitting closely over it by being pasted round its rim. The diaphragm may be pierced by a few small pin-holes, which greatly facilitates the sublimation. The pan is surmounted with a paper cap twelve or eighteen inches high, fitted closely to its top, and fastened by means of a cord passed two or three times round it. The apparatus is to be cautiously heated for ten or twelve hours on a sand- or still better on a metallic bath. The temperature is to be kept as nearly as possible at about 400° F., though towards the end of the sublimation it may be raised a few degrees higher. The crystals of pyrogallic acid pass up through the bibulous paper, which absorbs the empyreumatic oil by which they are always accompanied. Should the heat have been carefully regulated, the crystals, which are either large scales or needles, are perfectly white; should they be slightly coloured, which sometimes happens, they may be easily purified by a second sublimation. This method possesses the great advantage that a pound or more of the extract can be operated on at once; the apparatus is extremely cheap, and as it is not liable to break it may be used for any number of times. On one trial 1380 grains of dried extract yielded 69 grs. of perfectly pure crystals, and 74 grs. which were slightly coloured, in all 143 grs., or 10·3 per cent. Now as galls yield rather more than half of their weight of soluble matter, the quantity of pyrogallic acid obtainable from them by this process is very considerable. I think it right to mention, however, that on a previous trial, when the sublimation was not so carefully conducted, I did not obtain more than half this quantity.

The following are some of the leading characters of pyro-

gallic acid. It has a very bitter taste, resembling that of salicine. When pure it does not redden litmus paper; but if it has been sublimed at too high a heat, it is accompanied with a little of some volatile acid, which causes it to redden litmus slightly. It gives a deep indigo-blue colour with solutions of protosulphate of iron, but no precipitate falls. If the protosalt contains any peroxide, this colour soon changes to dark green; but if the salt is pure the deep blue colour remains for a considerable time. With persulphate of iron it gives a yellowish red; with perchloride a much brighter red, but in neither case any precipitate. When pyrogallic acid is dropt into milk of lime, a beautiful reddish purple colour appears, which however speedily changes to a dark brown. Caustic barytes produces a dark brown colour which quickly becomes black. Its reactions with salts of iron and milk of lime are the best tests for pyrogallic acid, and by these its presence even in very small quantity can be easily ascertained. It is very soluble in water, but its aqueous solution, if exposed to the air, speedily blackens. It is also very soluble in alcohol, though not so much so as in water. The taste of its alcoholic solution very much resembles laudanum. Dilute sulphuric acid first reddens pyrogallic acid and then blackens it. Iodine has no effect upon it. Dry chlorine instantly colours the crystals of pyrogallic acid bright red and then blackens them. Moist chlorine, when sent through a solution of pyrogallic acid, gives it a hyacinth-red colour, and evolves much muriatic acid; no precipitate fell, however, and when left to spontaneous evaporation it yielded no crystals, but left only a reddish gummy mass. Pyrogallic acid reduces the oxides of gold, silver and platinum to the metallic state, and precipitates them completely from their solutions. In order to test the purity of the pyrogallic acid I had obtained, it was dried at 212° F., and analysed in the usual way. 0·312 gram. gave 0·65 carbonic acid, and 0·1345 water.

Found.	Calculated.	
C 57·60	8 C = 611·480	= 57·61
H 4·78	4 H = 49·918	= 4·70
O 37·62	4 O = 400·000	= 37·69
100·00	1061·398	100·00

This result agrees closely with the calculated numbers given above.

I next endeavoured to form the hydrate of pyrogallic acid by dissolving some very pure crystals in a small quantity of water, and evaporating the solution *in vacuo* over sulphuric acid. It gave large white needles of a silky lustre.

Burnt with oxide of copper,—

I. 0·3265 gramme substance, dried *in vacuo*, gave 0·68 carbonic acid, and 0·138 water.

II. 0·2873 gramme, dried at 212° F., gave 0·600 carbonic acid, and 0·124 water.

	I.	II.	Calculated.
C	57·58	57·83	57·61
H	4·97	4·79	4·70
O	37·45	37·38	37·69
	100·00	100·00	100·00

Pyrogallic acid, therefore, does not form a hydrate.

Pyrogallate of Lead.

In order to determine the atomic weight of pyrogallic acid, the lead salt was prepared by adding a solution of pyrogallic acid to an excess of neutral acetate of lead in the cold. A copious white flocculent precipitate immediately fell. It was washed repeatedly by decantation, then thrown upon a filter and rapidly washed, the air being excluded as much as possible, and when pressed between folds of blotting-paper was dried *in vacuo*. When dried it was still nearly white, having only a slight shade of yellow.

I. 0·7985 gramme, dried *in vacuo*, gave 0·269 oxide of lead and 0·174 metallic lead = 57·16 per cent. oxide.

II. 0·731 salt gave 0·252 oxide and 0·153 lead = 57·02 oxide of lead.

III. 0·6402 gave 0·1712 oxide and 0·1815 lead = 57·28 per cent. oxide.

IV. 0·709 salt, dried at 212° F., gave 0·252 oxide and 0·143 lead = 57·27 per cent. oxide.

0·5685 salt gave, when burnt with oxide of copper, 0·504 carbonic acid and 0·117 water.

		Calculated.	
C = 24·51	8 C =	611·480 =	24·89
H = 2·28	4 H =	49·918 =	2·03
O = 16·03	4 O =	400·000 =	16·30
Pb O = 57·18	Pb O =	1394·500 =	56·78
100·00		2455·898	100·00

The mean of these determinations gives 1044 for the atomic weight of pyrogallic acid, which corresponds pretty closely with the calculated number 1061. It is evident also that these analyses give $C_8 H_4 O_4$ as the formula of pyrogallic acid; and not $C_6 H_3 O_3$, that of Berzelius. The formula $C_8 H_4 O_4$ is that found by the late R. C. Campbell, as stated in Liebig's Geiger; but I am not aware that the details of his analysis have ever been published.

When even a single drop of caustic ammonia is added to a

solution of pyrogallic acid, it becomes alkaline and assumes a dark brown colour. A great excess of ammonia was added to a solution of pyrogallic acid, which was then evaporated *in vacuo*. The acid crystallized in confused tufts of a dark brown colour; when pounded, however, its colour was only light brown. It did not give the least indication of ammonia when heated either with a strong solution of potash or with quick lime. When dried *in vacuo* and subjected to analysis,

I. 0·4620 substance gave 0·9255 carbonic acid, and 0·201 water.

II. 0·3141 substance, also dried *in vacuo*, gave 0·6314 carbonic acid, and 0·1405 water.

I.	II.
C 55·38	C 55·58
H 4·83	H 4·96
O 39·79	O 39·46
100·00	100·00

Now pyrogallate of ammonia should have given only 44·44 per cent. carbon, and 6·34 per cent. hydrogen.

The substance of number II. was prepared at a different time from number I.; and in its preparation a still larger excess of ammonia was employed. The reactions of the supposed pyrogallate of ammonia with salts of iron and milk of lime were exactly the same as those of ordinary pyrogallic acid. It is evident, therefore, that pyrogallic acid does not combine with ammonia, but is slightly oxidized when brought in contact with it.

The addition of a little potash also rendered solutions of pyrogallic acid alkaline and even darker coloured than ammonia does. The colorization takes place first at the surface of the liquid, and is evidently the effect of oxidation. When evaporated *in vacuo* it became a black gummy mass, which showed no disposition to crystallize. When this black mass was dissolved in water, in which it is very soluble, and treated with sulphuric acid, it effervesced, apparently from the escape of carbonic acid. It also gave off the vapours of acetic acid in abundance. These were easily recognisable by their smell, and by their immediately reddening litmus paper when held over them. When the solution was very concentrated, a little of a dark brown matter precipitated; but if the solution was at all dilute no precipitate appeared. I made an unsuccessful attempt to collect this precipitate on a filter, and to free it from adhering sulphuric acid by washing it with cold water. The whole of the black matter was speedily dissolved and passed through the filter. Soda produced similar effects on pyrogallic acid. It is plain, therefore, that pyrogallic acid is

decomposed by the alkalies, but does not combine with them, and that its acid properties, if indeed it possesses any, are very feeble. In this and some other respects it closely resembles pyromeconic acid.

When pyrogallic acid is dropped into acetate of copper, it causes a dark brown precipitate, which however quickly becomes black, and is very soluble. When we attempt to collect it on a filter and to wash it, the greater portion of the salt is dissolved by the water. The liquid when it first passes through the filter is colourless, but on standing a few minutes it becomes dark brown and slowly deposits a new precipitate. The compound first formed appears to be decomposed by the water.

When pyrogallic acid is added to a solution of bichromate of potash, it immediately turns it yellowish brown, and then dark brown till the liquid is almost opake, but no precipitate falls.

XXIII. *On some Astringent Substances as Sources of Pyrogallic Acid. By Dr.* John Stenhouse.

Read November 15, 1842.

CHEMISTS have usually divided the varieties of tannin which occur so abundantly in the vegetable kingdom, into two kinds; those which give *black* and those which give *green* precipitates with salts of iron. The propriety of this distinction has of late been called in question by Berzelius, who seems to think that the tannic acid in all plants is essentially the same; and that the green and gray colours of the precipitates with salts of iron are owing to the presence of free acid. Professor Liebig appears also to hold a similar opinion. Berzelius states at 116th of his *Rapport Annuel* for 1841, on the authority of C. H. Cavallius, "that the tannic acids which give green precipitates with sulphate of iron, give blue precipitates with acetate of iron, and that their green combinations are rendered blue by the addition either of small quantities of acetate of lead, by a little alkali, or even by a great excess of gelatine." He also states that the lead compounds of those species of tannin which give green precipitates with salts of iron are rendered blue by the addition of a little sulphate of iron. He likewise affirms that when a solution of any of the tannins which give green precipitates remains in contact for some time with chips of iron, a blue instead of a green precipitate is obtained, and that its blue colour is changed to green by the addition of acetic acid. These statements have induced Berzelius to conclude that the giving green or black precipitates with salts of iron is not a distinctive

character for any species of tannin, as these precipitates are convertible into each other; bases rendering them black or blue, and acids gray or green. A few experiments which I have made have, however, given somewhat different results from those of Cavallius.

A solution of the tannin of catechu was prepared by macerating a large quantity of catechu in a very little cold water; it was therefore quite free from catechin. A portion of this solution was allowed to remain for some days in contact with a quantity of iron chips; it assumed a dirty, grayish black colour, which, however, did not at all resemble the blue-black colour which nut-galls, oak, bark, &c. exhibit when similarly treated. The precipitate did not become green when a little acetic acid was added to it, but it dissolved in an excess of acid, and on being neutralized with ammonia a purple gray precipitate appeared. Tannin of catechu gave a dull grayish black precipitate with acetate of iron. With neutral acetate of lead it gave a light yellow precipitate, which on the addition of sulphate of iron assumed a dark gray colour, much lighter than the preceding. Basic acetate of lead gave similar results. Chloride of iron gave an olive green; perchloride an olive brown, and protonitrate a yellowish green precipitate. Tannin of catechu, when treated with acetic acid and sulphate of iron, gave a dark olive precipitate.

The tannin of larch bark, which gives a light green precipitate with protosulphate of iron, gave with acetate of iron a purplish black precipitate, which on standing for a day or so assumed a dark lead colour. When treated first with acetate of lead and then with sulphate of iron it gave a grayish purple precipitate. When mixed with a little acetic acid it gave a dark gray precipitate on the addition of sulphate of iron. Chloride of iron produces a grayish brown, and nitrate of iron an olive brown precipitate.

The tannin of gum kino gave with protosulphate of iron a dark green, and with acetate of iron a purplish black precipitate, which on standing changed to grayish black. With protochloride and protonitrate of iron dark green precipitates, which quickly changed to grayish brown. The effect of alkalies on all these precipitates was only to deepen their colours, but not to change any of them bluish black.

The tannin of alder bark, birch bark and tormentil root, gave purplish black precipitates with acetate of iron, which however on standing became grayish black, and their reactions with the inorganic salts of iron were almost identical with those of kino, catechu and larch bark, and wholly dissimilar with those of galls, sumach, valonia, &c. Very good ink of a

bluish black colour may be made from nut-galls, oak bark, sumach, valonia, divi-divi, &c.; but the tannin of catechu, kino, larch, birch and alder barks, &c., are wholly unfit for this purpose. Indeed the only salt of iron which gives pretty nearly the same coloured precipitates with either species of tannin is the acetate, but even these, though at first bluish black in the case of the green tannins, become in a day or two grayish black, and their reactions with the sulphate, chloride and nitrate of iron have no resemblance whatever to those of the black tannins. The old distinction, therefore, which divides the astringents into those which give black, and into those which give green precipitates with the inorganic salts of iron, appears, so far as it goes, to be perfectly just, as these precipitates are not convertible into each other, as affirmed by M. Cavallius. There is, however, good reason for believing that some of the varieties of tannin, which even agree in their reaction upon salts of iron, and in their characters generally, are still by no means identical substances. In this respect there is considerable analogy between the varieties of tannin and the different fatty acids.

It is much to be regretted that we are unable to procure tannin in a state of purity from any other source than nut-galls. When pounded galls are treated by Pelouze's method, with hydrated æther, in a displacement apparatus, the liquid on standing separates into two strata, the lowest of which contains tannic acid in a state of purity.

When, however, oak bark, valonia, sumach, gum kino, catechu, &c. are treated with æther in a similar manner, only one stratum of liquid is obtained. Pelouze's process is therefore inapplicable to these substances. This is the more to be regretted, as from the extreme facility with which tannin decomposes when in contact with moisture, we are unacquainted with any good way of obtaining it in a pure state from any of the other astringent substances; and consequently, with the exception of nut-galls, little progress has been made in the investigation of these bodies.

It has been already mentioned that the tannin of galls and gallic acid are the only substances which, when distilled, are known to yield pyrogallic acid—a substance whose characters are so well marked that it can easily be recognized. It struck me, therefore, that this circumstance might be employed as an easy test for the presence of gallic acid; and also enable us to ascertain when the tannin these substances contained was similar or otherwise with that of nut-galls. With this view I was induced to subject a number of the astringent matters to examination. The first in the order was sumach.

Sumach, which is so extensively employed in Great Britain by dyers and leather-curriers, consists of the small branches of the *Rhus coriaria*. A quantity of sumach was digested with hot water, filtered and evaporated to dryness. The dried extract thus obtained was subjected to distillation. The liquid which passed into the receiver, though it gave no crystals of pyrogallic acid, obviously contained that substance, as it exhibited all its characteristic reactions. The pyrogallic acid was prevented from crystallizing by the empyreumatic oil and other impurities by which it was accompanied. It seemed not improbable, therefore, that sumach contained gallic acid, and that perhaps its tannin was also similar to that of galls.

The first step taken, therefore, was to examine sumach for gallic. Several pounds of sumach were repeatedly boiled with water and then filtered. The tannin contained in the liquid was precipitated by solution of glue and separated by filtration. Its quantity was very considerable. The clear liquid was evaporated to the consistence of an extract, and treated with hot alcohol. The greater portion of the spirits was recovered by distillation, and the residue set aside to crystallize. After some days, as no crystals made their appearance, the alcoholic solution was evaporated to dryness on the water-bath. It was then introduced into a stoppered bottle and repeatedly agitated with æther; almost the whole of the æther was distilled off, and the residue left to spontaneous evaporation. Abundance of reddish coloured crystals soon appeared. They were purified by repeated digestions with animal charcoal and successive crystallizations. The crystals were then perfectly colourless and possessed the silky lustre of gallic acid, with which acid their reactions with salts of iron and other reagents completely corresponded. When distilled they yielded abundance of pyrogallic acid. They were dried at 212° F. and subjected to analysis.

I. 0·2932 gramme substance gave 0·5315 carbonic acid, and 0·963 water.

II. 0·2824 gave 0·508 carbonic acid, and 0·956 water.

	I.	II.	Calculated.
C	50·12	49·73	7 C = 49·89
H	3·64	3·76	3 H = 3·49
O	46·24	46·51	5 O = 46·62
	100·00	100·00	100·00

These results approach pretty closely the calculated numbers of hydrated gallic acid given above.

In order to determine the atomic weight of the acid, the basic gallate of lead was formed by adding a solution of the

acid obtained from sumach to an excess of boiling acetate of lead. It precipitated as a yellow, slightly crystalline powder, and was also dried at 212° F.

I. 0·803 salt gave 0·456 oxide and 0·142 metallic lead = 75·84 per cent. oxide of lead.

II. 0·6972 gave 0·332 oxide and 0·186 metallic lead = 76·35 oxide.

Now the bibasic gallate of lead C^7 H O^3 + 2 Pb O contains 76·69 per cent. oxide of lead; therefore there can be no doubt that it was the salt analysed, and that gallic acid, therefore, occurs to a considerable extent ready formed in sumach.

I next proceeded to examine the tannin. In order to obtain the tannin of sumach free from gallic acid, I macerated a very considerable quantity of sumach in a very little cold water, filtered the liquid, and threw down the tannin it contained by adding to the solution about half its bulk of sulphuric acid by small quantities at a time. The precipitate, which had a brownish yellow colour, was tolerably abundant. It was collected on a cloth filter, washed with a little cold water, and strongly compressed so as to remove as much of the sulphuric acid as possible. It was then dried and distilled. It yielded crystals of pyrogallic acid as freely as the same quantity of tannin of galls would have done. The products of the distillation of tannin from both these sources are, therefore, the same.

In order to see if the analogy extended any further, I was induced to try if the tannin of sumach would be converted into gallic acid by being boiled with dilute sulphuric acid, as is the case with tannin when similarly treated. A second portion, therefore, of the tannin of sumach precipitated by sulphuric acid and purified like the former, was boiled for an hour with a mixture of two parts water and one of sulphuric acid. It was filtered while hot. When the liquid cooled, an abundant crop of hard, dark brown crystals appeared. They were collected on a filter and washed with a little cold water, then pressed and dried. They were repeatedly dissolved in small quantities of water, and boiled with purified animal charcoal till they were perfectly colourless. When subjected to analysis,

I. 0·279 acid gave 0·505 carbonic acid, and 0·945 water.

II. 0·3145 gave 0·5675 carbonic acid, and 0·1056 water.

	I.	II.	Calculated.
C	50·04	49·78	7 C = 49·89
H	3·76	3·73	3 H = 3·49
O	46·20	46·49	5 O = 46·62
	100·00	100·00	100·00

These results again agree with the numbers of hydrated gallic acid.

The bibasic gallate of lead was also formed with another portion of the acid in the way already described.

I. 0·690 salt gave 0·153 oxide and 0·3448 lead = 76·18 per cent. oxide.

II. 0·7415 salt gave 0·1745 oxide and 0·3635 lead = 76·34 per cent. oxide.

There can be no doubt, therefore, that the acid produced by the action of sulphuric acid on the tannin of sumach is the gallic acid, precisely as is the case with the tannin of galls. Another portion of the tannin of sumach precipitated also by sulphuric acid, and which had been freed as much as possible, by being washed and compressed, from any adhering acid, was kept well moistened in an open vessel for more than five weeks at a temperature of about 70° F. It readily yielded crystals of gallic acid when treated with alcohol and æther in the way already described. Sumach, therefore, appears to approach the nature of nut-galls more closely than any of the other astringent substances. This fact is well known to Turkey-red dyers, who have long successfully employed sumach as a substitute for galls; as might be expected, a greater weight of sumach is required to produce the same effect, as the quantity of gallic acid and tannin contained in sumach is much less in proportion to its bulk than in nut-galls.

The effect of the action of sulphuric acid upon the tannin, both of sumach and of galls, varies very much according to the strength of the acid employed. When the preparation of gallic acid alone is our object, we succeed best by using acid diluted with seven or eight times its bulk of water. The digestion should be continued for a day or so, new quantities of water being added from time to time as the evaporation proceeds. When the digestion is finished, the liquid should be concentrated by a very gentle heat. Nearly the whole of the tannin is converted into gallic acid, which is deposited in crystals which are only slightly coloured, and therefore easily purified. If, on the other hand, more concentrated acid is used, the crystals are very dark-coloured, and require repeated digestion with animal charcoal, which occasions both trouble and loss. Besides, concentrated acid converts only about a half of the tannin into gallic acid. The other portion is changed into a dark-coloured pulverulent substance possessing decided acid properties, and very much resembling humus in appearance.

Action of Muriatic Acid upon Tannin.

Muriatic acid converts tannin into gallic acid in precisely

the same way as sulphuric acid does. If the muriatic acid is pretty dilute, and the digestion conducted with a moderate heat, the tannin is almost wholly resolved into slightly coloured gallic acid, and a very little only of the insoluble black matter appears. If, on the contrary, we employ an acid diluted with even three times its bulk of water, and continue the boiling for an hour, about half of the tannin is changed into very dark coloured gallic acid, and the rest is converted into the insoluble black matter already mentioned. In order to ascertain that the acid obtained by this process was really gallic acid, it was purified and subjected to analysis. It possessed all the reactions of ordinary gallic acid.

I. 0·2721 gramme substance gave 0·487 carbonic acid, and 0·0865 water.

II. 0·2902 gave 0·5235 carbonic acid, and 0·091 water.

	I.	II.	Calculated.
C	49·49	49·87	7 C = 49·89
H	3·53	3·48	3 H = 3·49
O	46·98	46·65	5 O = 46·62
	100·00	100·00	100·00

In order to determine the atomic weight of the acid its basic lead salt was prepared in the way already mentioned.

I. 0·758 salt gave 0·245 oxide and 0·307 metallic lead = 75·95 per cent. oxide of lead.

II. 0·771 salt gave 0·212 oxide and 0·347 metallic lead = 75·97 oxide per cent.

The calculated quantity of oxide of lead in the bibasic gallate is 76·69 per cent.

From these results there can be no doubt that the acid was gallic acid.

Tannin is precipitated from its solution by muriatic acid even more perfectly than by sulphuric acid, and it is a matter of indifference which of the two acids we employ in order to convert it into gallic acid. The only advantage attending the employment of muriatic acid is that by evaporating the mixture of the two acids nearly to dryness on the water-bath, the greater portion of the muriatic acid may be easily driven off

Nitric acid does not precipitate tannin from its solution, but almost immediately converts it with evolution of deutoxide of azote into very pure oxalic acid.

The pulverulent substance already mentioned as produced along with gallic acid by the action of muriatic and sulphuric acids upon tannin, has very much the colour of soot and is nearly tasteless. It is insoluble in cold water, and very slightly so in boiling water. When laid on moistened litmus paper,

however, it reddens it strongly. It consists of at least two substances, one of which only is soluble in hot alcohol, so that they may be easily separated by this means. They both dissolve very readily in alkalies, and decompose the carbonates when assisted by heat. When saturated with ammonia and rendered neutral by digestion, they give dark brown precipitates with salts of silver, copper, iron, lead, barytes and lime. Their alkaline solutions are dark brown, and they are completely precipitated by acids. These humus-like substances are produced by the action of the acids on the tannin only, for on boiling gallic acid with concentrated muriatic acid for several hours I did not succeed in obtaining even a trace of them. I am at present engaged in their further investigation.

Valonia.—The next of the astringent matters examined was valonia. It is the acorn of the *Quercus Ægilops*, and is imported in considerable quantities from the Levant for the use of the tanners. The dried extract of valonia prepared like that of sumach, when destructively distilled, gave no indication of pyrogallic acid. Valonia was next examined for gallic acid. A strong solution of it was precipitated by glue, and the clear liquid evaporated to an extract and heated with spirits of wine. The spirits of wine were distilled off, and the residue treated with æther exactly as sumach had been. A very small quantity of crystals was obtained. They exhibited the reactions of gallic acid on salts of iron and other reagents, and when distilled yielded crystals of pyrogallic acid. I have every reason to believe that these crystals were gallic acid, though from the smallness of their quantity I was unable to subject them to analysis. Valonia, therefore, may be regarded as containing a little gallic acid, but its quantity is so inconsiderable as probably not to amount to a thirtieth of what sumach contains.

The most concentrated solutions of valonia give a very scanty precipitate when treated with sulphuric acid; and a large quantity of valonia must therefore be employed to yield any quantity of tannin by this process. The precipitate has a bright yellow colour. When distilled it left a very bulky charcoal, and gave scarcely any empyreumatic products. The liquid which passed into the receiver was nearly colourless, and did not give the least indication of pyrogallic acid. The tannin of valonia appears, therefore, essentially different from that of nut-galls.

Oak Bark.—The extract of oak bark when dried and distilled, also gave no indication of pyrogallic acid. I then endeavoured to obtain gallic acid by treating a decoction of oak bark in the way already described. Though I operated on

considerable quantities, such as six and eight pounds, I did not succeed in the course of several trials in obtaining any crystals of gallic acid. I apprehend, therefore, that if oak bark contains any gallic acid at all, it must exist in very minute quantity. The tannin of oak bark when precipitated by sulphuric acid had a reddish brown colour. When subjected to distillation it gave no indication of pyrogallic acid. The tannin was also boiled with dilute sulphuric acid. It became darker coloured and nearly insoluble either in hot or cold water. It was a little more soluble, though very slightly so, in alkaline leys. On the addition of an acid a few reddish flocks precipitated. Spirits of wine also dissolved a little of it, and assumed a light red colour. The tannin of oak bark appears, therefore, also to differ from that of nut-galls.

Divi-divi.—The astringent substance by some called Divi-divi, by others Libi-divi, has of late years been imported into Great Britain from Carthagena in considerable quantity. It is the pod of a leguminous shrub which grows to the height of between twenty and thirty feet. Professor Balfour informs me that its botanical name is *Cæsalpin coriaria*. It is a native of South America, and is noticed by Dr. McFadyen in his Flora of Jamaica, as occurring in that island. The pods of this shrub, which form the divi-divi of commerce, are of a dark brown colour, nearly three inches long and about half an inch broad. They are very much curled up, as if they had been strongly dried; and contain a few flattish seeds. The taste of divi-divi is highly astringent and bitter. The astringent matter is contained only in the outer rind of the pod; the inner skin, which incloses the seeds, is nearly tasteless. The pods are often perforated with small holes, evidently the work of some insect. The aqueous solution of divi-divi gives a copious precipitate with gelatine, and strikes a deep blue with persalts of iron.

When dried extract of divi-divi was distilled, the liquid which passed into the receiver, though it gave no crystals of pyrogallic acid, evidently contained that substance, as it exhibited all its characteristic reactions.

When divi-divi was treated for gallic acid in the way I have already described, I easily succeeded in obtaining a considerable quantity of reddish-coloured crystals, which, when purified like the others with animal charcoal, became perfectly white. They had the usual reactions of gallic acid, and yielded pyrogallic acid when distilled.

When dried at 212° F. and subjected to analysis,—

I. 0·3034 gramme acid gave 0·550 carbonic acid, and 0·1018 water.

II. 0·3052 gave 0·5505 carbonic acid and 0·1012 water.

	I.	II.	Calculated.
C	50·12	49·87	7 C = 49·89
H	3·72	3·71	3 H = 3·49
O	46·16	46·42	5 O = 46·62
	100·00	100·00	100·00

In order to determine the atomic weight of the acid, I formed the bibasic gallate of lead.

I. 0·706 of this salt gave 0·3325 lead, and 0·1802 oxide = 76·25 per cent. oxide of lead.

II. 0·887 salt gave 0·315 lead and 0·340 oxide of lead = 76·58 per cent oxide.

Now the bibasic gallate of lead C^7 H O^3 + 2 P bo contains 76·69 per cent oxide of lead; there can, therefore, be no doubt that it was the salt analysed, and that gallic acid occurs to a considerable extent ready formed in divi-divi.

Sulphuric acid throws down a very scanty dark brown precipitate, even in highly concentrated solutions of divi-divi. When dried and distilled, it did not yield any trace of pyrogallic acid, and left a very bulky charcoal. The tannin of divi-divi appears, therefore, essentially different from that of nut-galls.

Mr. Harvey informs me that a few years ago some calico-printers endeavoured to employ divi-divi as a substitute for galls, but the large quantity of mucilage it contained rendered it unfit for this purpose.

It is at present pretty extensively employed in the tanning of leather, as the quantity of tannin it contains is considerable, and the presence of mucilage is not injurious to that process.

Gum Kino.—The species of kino which I examined was the African variety. I was unable to detect in it any trace of gallic acid. Sulphuric acid threw down the tannin of kino as a bulky dark red precipitate. When distilled, it gave scarcely any volatile products, and no trace of pyrogallic acid. When digested with nitric acid, gum kino was wholly converted into oxalic acid.

Catechu.—It was the light-coloured cubical variety of catechu that I employed. It does not contain any gallic acid, but catechin and a variety of tannin which gives olive green precipitates with salts of iron. Sulphuric acid throws down the tannin of a brownish yellow colour. When boiled with dilute sulphuric acid, it becomes dark brown. Like the tannin of oak bark, it is insoluble either in cold or boiling water. When boiled in strong alkaline solutions, it only dissolves to a very small extent. It is also insoluble in alcohol and æther.

When distilled, the tannin gave no indication either of pyrogallic acid or of pyrocatechin.

Catechin, which is the part of catechu insoluble in cold water, when distilled, yielded the pyrocatechin of Zwenger in considerable quantity. So far as I examined it, pyrocatechin appeared to possess the properties ascribed to it by that chemist.

In conclusion, I may mention that this is only the first of a series of papers on the astringent substances.

Glasgow, Oct. 26, 1842.

XXIV. *On some new cases of Voltaic Action, and on the Construction of a Battery without the use of Oxidizable Metals.* By Alexander R. Arrott, *Esq.*

Read November 15, 1842.

HAVING been for some time engaged in examining into certain remarkable voltaic actions occurring in cases hitherto unobserved, or at least not followed out so fully as their importance seems to demand, I am induced briefly to communicate the results of my inquiries, hoping they may not prove uninteresting to the Society.

It is a fact known to every one who has carefully observed the phænomena attending chemical decomposition by means of electricity, that the electrodes immersed in the solution undergoing decomposition, acquire the power of producing a current in the opposite direction to that previously passing through them, when they are made to touch each other without being removed from the liquid.

This effect has generally been ascribed to a power supposed to be acquired by the metals, of producing a current independently of any action of the liquids beyond that of simply completing the circuit, and has been called "polarization of the electrodes."

Becquerel was the first who advanced the opinion, that the effect was due to the alteration produced in the liquid by the current causing decomposition. He supposed that the current was a consequence of the combination of the acid and alkaline produced at the positive and negative surfaces; but it will be found that the most powerful acids and alkalies are incapable of producing a current, unless they readily undergo some other change than that which takes place when an acid and alkali combine as such. It has often been shown, that sulphuric acid and potash, for example, are nearly or altogether

incapable of producing this effect; iodic, chloric, chromic, or, as in the beautiful arrangement of Becquerel, nitric acid, with an alkali, produce a powerful current, but in these cases the action is very different from that which takes place in simple neutralization of an acid by an alkali.

I have observed, that a current is produced in many cases where, from the nature of the liquids, no current can be supposed to arise either from the union of an acid and an alkali, or from the action of the liquids on the metals employed. Thus I found, that solutions of a per- and protosalt of iron, produced a current when they were allowed to touch each other, and also made to communicate by means of platina; the persalt becoming deoxidized and the protosalt oxidated.

It seemed that in this case the current was due to the oxidation and deoxidation of the liquids, by means of the elements of water which was decomposed, and it appeared probable that, if substances were used capable of exerting a greater attraction for the oxygen and hydrogen, that a proportionally greater effect would be obtained. With this view, I tried solution of chlorine, and found that the effect was very much increased. I next tried iodine in solution in water, and also in iodide of potassium: the effect was very feeble; and this is exactly what we ought to expect, for iodine has nearly an equal tendency to unite with oxygen and hydrogen, as appears from the mode in which it decomposes water. I was not aware at the time of making these experiments, that Schoenbein had obtained the current from chlorine.

We have an extremely simple and beautiful illustration of these actions in the case of salts of iron. If two tubes be stopped at one end with plaster of Paris, and filled one with per- and the other with protosulphate of iron, and both immersed in a vessel containing dilute sulphuric acid, on adding red prussiate of potash to the persalt, and sulphocyanide of potassium to the other, no change takes place; but if we connect the two solutions by means of a slip of platina foil, we have instantly indications of the oxidation of the one, and deoxidation of the other. I have also constructed an apparatus in the form of a battery, which, while it serves to illustrate the action in question, may, I think, prove both convenient and economical as an instrument of research in ordinary galvanic experiments. It consists of six small circular jars, within which are fixed tubes of baked clay, or porous earthenware. Small cylinders of platina foil, 0·6th inch diameter, and 1·5 inch long, were placed in the porous tubes, and outside these larger cylinders of 1·8th inch diameter, and 1·5th inch long. The whole was then formed into a series, by connecting the

outer cylinder of the first jar with the inner one of the second, and so on; the porous tube was then filled with strong nitric acid, and the jar with solution of sulphuret of potassium. The arrangement is exactly similar to Daniell's constant battery, except that the metallic surfaces are entirely of platina.

With an instrument of the above dimensions, I have obtained by means of a voltameter, 0·5th cubic inch of the mixed gases in a minute, and that action continues for some hours, with very little diminution.

I find that the substances capable of producing a current in similar circumstances, are very numerous; for example, per- and protosalts of iron, tin, and manganese, an alkaline sulphuret hyposulphite, hypophosphite or a hydracid on the one side, and chlorine or chromic or nitric acid on the other.

The intensity of the effect is, however, very various in these different combinations; thus, with salts of iron it is very feeble; while with chlorine or nitric acid and an alkaline sulphuret, the intensity is such, that the induction of one pair of plates is sufficient to cause the decomposition of water.

Each of the combinations, it will be observed, is formed of an oxidating and a deoxidating substance, and the change which takes place is similar in all of them; the oxidating substance is reduced and the deoxidating is oxidated.

If we employ only one substance, for example—chlorine, the chlorous element of the water finding nothing with which it can unite, is evolved; but in that case the intensity of the action is very much reduced.

The mode in which the experiments were performed was very simple. A small vessel of baked clay was cemented inside a wine glass; the respective liquids were then poured into this vessel and into the glass, till they stood at the same level; in this way they were in free liquid contact, while their actual mixture proceeded with extreme slowness; metallic plates, which were in all cases of platina, were then plunged into the solutions; the plates had been carefully cleaned with nitric acid, then with potash, and washed with water.

I now proceed to state the conclusions at which I have arrived, as regards the law which regulates the action in the ordinary voltaic battery, and in the arrangements above mentioned.

This I find to be in strict agreement with that of ordinary mechanical forces, viz. that the action and reaction are equal and opposite. When a metal is reduced from its solution, the equal reaction seems to follow as a corollary to the law of definite electrolyzation, and in cases where no solid substance is deposited, the same law holds.

In order to prove this, and also to show that the effect is not dependent on any particular state of the metals, a porous vessel was filled with a *mixture* of strong solutions of proto- and per-sulphates of iron; this vessel was, then placed in another filled with the same mixture, a platina plate was plunged into each vessel, and the circuit completed by a delicate galvanometer; not the slightest effect was produced; the plates were then put in communication with the poles of a common battery, and the amount of current which passed measured by means of a voltameter. No gas was evolved in the solutions, nor was any iron reduced, but the persulphate increased in quantity at one side, and the protosulphate at the other. When 80 measures of gas were collected, the battery was removed, and the plates being connected by the galvanometer as at the beginning of the experiment, a powerful current was produced in a direction the reverse of that of the battery; the effect was the same whether the same or fresh plates were used, and if they were simply washed with water, they might be moved from one vessel to the other, without producing the slightest effect on the current, provided their connexion with the galvanometer was also changed. The arrangement was again connected with the battery, in such a manner that the current should move in the solutions in the opposite direction to the former battery current, 80 measures of gas were again collected, and the battery being removed, not the slightest current was observed on connecting the plates with the galvanometer, but every thing was in the same state as at the commencement of the experiment. The power of the solution to produce the current, gradually diminishes, but is not entirely destroyed until the second or return current becomes equal in amount to the first. The quantity of the *return* current cannot be measured correctly, without using the battery to enable it to pass quickly; because, from the extreme slowness of the action towards the end of the experiment, the solutions unavoidably mix, and thus cause great error in the amount. A similar experiment was tried with nitric acid, containing a large quantity of the lower oxides of nitrogen with precisely similar results.

Where the circuit is entirely metallic, but not homogeneous, we have also a return current; for the heat produced in a thermoelectric arrangement, causes a current the reverse of that which produces it; but we cannot in this case determine the amount, from the impossibility of retaining the heat produced, and of preventing it from extending to those parts which ought to remain cold; the same may be the case also in a homogeneous circuit, but from the extremely low inten-

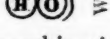
sity, which is only equal to that necessary to cause the current to pass through it, we are unable to observe it.

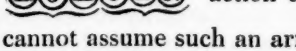
From these and other observations of a similar kind, I believe it may be stated as a general law, that when a current passes through a series of conductors, it induces a state of things, capable of producing a current equal to itself in amount, and opposite in direction; provided the changes produced are permanent.

This law can be proved to hold in all cases where a liquid forms part of the circuit, with the single exception of the case where two pieces of the same metal communicate by means of one of its salts; here the phænomena are the same as if the metallic circuit were complete. (Faraday.)

These results appear to show that there is something of the nature of a force transmitted through the circuit, and the phænomena of tension lend great support to this idea, for here we have bodies actually put in motion.

If now we suppose each chemical molecule to be capable of exerting an attractive force on every other molecule in its vicinity, the phænomena of the voltaic circuit are precisely what should result from such an attraction, and voltaic action appears to be chemical action under another form; the action in one case taking place between molecules in contact, or at extremely small distances, and in the other between those at a considerable and sensible distance.

If any number of molecules of different substances be placed near each other, and in such a state as to admit of their free motion, they arrange themselves so that their attractive forces produce a state of equilibrium, and till this state is attained the molecules are in a constrained condition. Thus when chlorine, hydrogen and water are brought into contact, the hydrogen and chlorine unite to form hydrochloric acid, and this is the state of equilibrium. The mode in which this state is attained seems to be as follows:—(Fig. 1.) 

; the atom of Cl unites with the H previously in combination with the O as water, while the O unites with the free H, and Cl H and H O are formed; if, however, the H and Cl are at some distance from each other, as when separated by water, the (Fig. 2.) 

action cannot take place, for the molecules cannot assume such an arrangement as would form a complete circuit, without which they cannot exert their attractions, but if H and Cl be united by a metal (Fig. 3.)

a body of an atomic constitution similar to the liquid, the circuit is completed, H Cl is formed, and equilibrium restored. The attraction which was before exerted between H and Cl was unobserved on account of their extreme nearness, but is now continued through the whole length of the circuit, and we have thus the means of observing the phænomena to which it gives rise.

If C l be the only free element, the molecules arrange themselves thus:—(Fig. 4.)

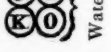
, the Cl and H unite, and the O is set free; if in place of Cl and O being in contact at the moment of the evolution of O, they are at some distance, the intervening space being occupied by a metal, we have the same phænomena as in the first case, except, that the O finding nothing with which it can unite, is set free at the surface of the metal; the action in this case proceeds much more rapidly than when no metal is used, in consequence of the great attraction between the zincous and chlorous atoms of the platina, for the attraction throughout the circuit is equal to the most powerful exerted at any part of it. It is not necessary that the atoms acting in this manner should be elementary substances, for compound substances, such as cyanogen, many neutral salts and organic substances act in the same manner.

The result of the action is the same, whether we simply mix the liquids, or form them into a voltaic circuit as above described. If, for example, we mix one equivalent of Cl and Sn Cl, one equivalent of Sn Cl_2 is formed. If, instead of mixing the solutions, we place them in porous vessels, immersed in hydrochloric acid, and connect them by a slip of platina, the result is the same as before, and the quantity of acid remains the same, having served merely as the means of connecting the solutions, and might be dispensed with, were it not, that the unavoidable mixing which takes place when the solutions are in contact, renders the result very unsatisfactory. If, in place of the above-mentioned solutions, we substitute the per- and protochloride of iron, the formation of per- and protochloride continues till the quantity of these salts is equal in the two vessels.

It thus appears that the result is the same as would be produced by diffusion.

The action as before mentioned is similar with H and Cl; with Cl and HO, HS, HI, KO, KS, KI, we have a chloride

of hydrogen, or of the metal formed, and the combined radical is evolved. This law is a general one, and holds good equally in ordinary chemical action; but here the result is modified from the circumstances in which the action takes place. Thus when Cl is added to K O, no oxygen is evolved; but this disappearance of the oxygen is entirely a secondary result; the oxygen at the moment of its evolution is in contact with Cl and KO, by which it is absorbed, giving rise to the chlorate of potash: but no such result can occur in the voltaic arrangement; for the oxygen, at the moment of its evolution, is not in contact with Cl, and therefore appears as gas. Another difference between voltaic and chemical action is, that in the former, substances unite which are without action on each other when simply mixed, for example—oxygen and hydrogen; but this arises from the powerful attraction of the molecules of the platina, re-acting on the hydrogen and oxygen. The intensity is thus raised to the point necessary to cause combination.

It will now be evident why no current should result from the union of an acid and an alkali; thus if hydrochloric acid and potash be in contact, we have simply an exchange of the elements (Fig. 5.) 

Cl unites with K, while the liberated O unites with the H of the hydrochloric acid, and the current is confined within the four elements, which cannot in this case be separated; the same is true of sulphuric acid, substituting SO_4 for Cl. Nitric, chromic and several other acids are capable of acting in a very different manner from this. The whole atom of acid $NO_6 + H$ is capable of acting in the same manner as Cl, uniting with the basyle of the substance in contact with it, and evolving the radical, as in the pile of nitric acid and potash of Becquerel, but in this case the acid is reduced to the state of peroxide of nitrogen or nitric oxide. The increase in the intensity of the action, by using potash in contact with nitric acid, seems to be due to the affinity of the potash, for an additional quantity of oxygen and the formation of peroxide of potassium, which is immediately decomposed by the water; on substituting caustic barytes, no oxygen is evolved.

The changes which take place when organic substances are arranged so that a current is formed, afford an interesting subject for inquiry, and it appears probable that many of the effects described as catalytic, are the result of actions of this nature; for it is not necessary that the substance connect-

ing the liquids should be a metal; any conducting substance will answer the same purpose; nor is it necessary that the substance should have a sensible size, for a single atom may produce a new arrangement of the molecules of the substance with which it is in contact, as in the case of platina with oxygen and hydrogen, when these substances are mixed, by the intensity of the attraction of its atoms, and this arrangement will depend on that of the substance causing decomposition; the arrangement of the atoms composing the ordinary molecules being similar in both.

It would thus appear that voltaic action is nothing more than chemical action taking place in circumstances that enable us to observe many of the phænomena to which it gives rise, and which we have no means of observing in ordinary cases; and that chemical action is the result of the tendency of the molecules to arrange themselves in a state of equilibrium, in the same manner as ordinary mechanical forces.

XXV. *On Æthogen and Æthonides.* *By* William H. Balmain.

Read December 6, 1842.

AT the commencement of the present year I made some experiments, with the hope of obtaining compounds of boron and silicon with nitrogen; and was successful so far as to obtain compounds consisting of boron and nitrogen together with certain metals, which are possessed of some very remarkable properties. The results of these experiments, with some remarks upon their bearing upon the science of chemistry, and a few facts proving the existence of analogous compounds of silicon and nitrogen, were published in the Phil. Mag. for October, 1842. Since that time I have succeeded in isolating the compound of nitrogen and boron, and have given it the name of Æthogen, from *αἴθων* and *γείνομαι*, because it produces, by uniting with the metals, compounds which glow with a peculiarly beautiful phosphorescent light when heated before the blowpipe in the oxidizing flame. And I think its compounds may with propriety be named Æthonides.

Preparation of Æthogen.—Heat to redness seven parts of finely powdered anhydrous boracic acid with nine parts of melon, in a crucible lined with charcoal; and immediately the crucible is sufficiently cool to admit of being handled, rapidly

transfer the light coherent powder which will be found in the interior, to a perfectly dry well-stoppered bottle.

Properties.—A white powder, light as prepared magnesia, infusible, and fixed at a white heat. Heated before the blowpipe it burns rapidly, giving the flame a green colour, but without phosphorescing. Exposed to air for a few seconds and then heated in a tube, it yields a palpable quantity of ammonia. Heated with hydrate of potass, it yields ammonia abundantly. It is not altered by hydrogen at a low red heat, nor by chlorine at ordinary temperatures, nor by the vapour of iodine; and it is insoluble in water, but communicates to it an alkaline reaction. It is decomposed with effervescence by nitric and sulphuric acids, and there remains after evaporation boracic acid. It deflagrates with chlorate of potass and with nitre. Heated to redness with potassium and zinc it yields æthonides of those metals.

Æthonide of Potassium. Preparation.—Take seven parts of finely powdered boracic acid and twenty parts of cyanide of potassium, free from water, and, as far as possible, from cyanate of potass and iron; and having lined a Hessian crucible with a paste of powdered charcoal and gum, and heated it until all water has passed away, place the mixture in the crucible, cover it by inverting and luting a smaller crucible over it, and heat it to whiteness for an hour: it is advisable to use a crucible as a cover, that there may be sufficient room for spurious sublimation, and the rent-hole should be bored in the bottom of this crucible and not in the luting at the side; and further to avoid the penetration of oxygen to the materials, it is well to line the upper in like manner with the lower; or, by heating together potassium and æthogen avoiding an excess of potassium, and heating the result with nitric acid to free it from excess of æthogen.

Properties.—A light white solid, infusible and insoluble even when heated in water, in solution of potass, hydrochloric acid, sulphuric acid (strong and diluted), nitric acid, and solution of chlorine; it is not altered upon exposure to air, nor does it affect the most delicate turmeric paper when placed upon it in a moist state. Heated with hydrate of potass or soda, it yields ammonia abundantly. In the deoxidizing flame of the blowpipe it is not altered, nor does it communicate any colour to the flame: but in the oxidizing flame it gives a strong green colour, and gradually fuses, yielding a perfect bead which is transparent, hot and cold; and when placed with a drop of water upon test papers, turned turmeric brown and red litmus blue. When the outside flame impinges upon a large

surface of the substance in powder, as when a glass tube soiled with it is held at the extreme point of the flame, it presents a beautiful green phosphorescence, owing no doubt to the formation of boracic acid at the surface, and if it be removed to the inner flame, the centre will incandesce, while the outer edges, where it meets with the oxygen of the air, will still yield the beautiful elegant green. When thrown upon fused chlorate of potass it deflagrates with a soft green light, and it will also deflagrate with nitrate of potass. It is not altered by being gently heated with potassium or sodium, nor when heated before the blowpipe on charcoal with lead, zinc, &c. Chlorine has no action upon it at a low red heat, and iodine, sulphur and corrosive sublimate may be sublimed from it without decomposing it. It is not decomposed by hydrogen at a red heat, but below that temperature is decomposed with the evolution of ammonia by the vapour of water, or by any substance which will yield water, as hydrate of potass, hydrate of lime, common clay, hydrated phosphoric acid and the rhombic phosphate of soda. It is not decomposed by hydrochloric acid at a low red heat, and I think it is not altered by hydrofluoric acid, for a small portion of it was mixed with a large quantity of fluorspar, with more than sufficient sulphuric acid to make it all into hydrofluoric acid, and heated as long as fumes passed off, when, after the sulphate of lime had been washed away with dilute nitric acid, it still yielded ammonia with hydrate of lime.

Æthonide of Zinc. Preparation.—Heat together, to whiteness, in a lined crucible, one part of anhydrous boracic acid and two and a half parts of cyanide of zinc—or heat finely granulated zinc with æthogen to the temperature at which zinc sublimes, and wash the result with nitric acid.

Properties.—A white solid resembling the last, gives ammonia abundantly when heated with a mixture of hydrate of lime and carbonate of potass, and is insoluble (with or without heat) in water, sulphuric acid, hydrochloric acid, nitric acid, solution of potass and ammonia. It is not decomposed by chlorine or hydrogen at a *full red heat*, nor by corrosive sublimate, nor by potassium or sodium. Before the blowpipe it is infusible, but in the oxidizing flame communicates a green colour, and when at the outer edge emits a *very brilliant* bluish phosphorescence, which appearance it also produces when simply dropped into the flame of a spirit-lamp. Thrown on fused chlorate of potass, it deflagrates with a faint blue light.

Æthonide of lead may be obtained by heating chloride of lead with æthonide of zinc, or by heating boracic acid with

cyanide of lead, or by heating together lead and æthogen. It phosphoresces with a green light.

Æthonide of silver may be obtained by heating together chloride of silver and æthonide of zinc, or by heating together æthogen and silver. It is a light white solid, and is not acted upon by any of the re-agents with which it was tried, not even by chlorine or hydrogen at a full red heat. This compound phosphoresces with a peculiarly fine green light.

I believe I have obtained æthonides of several other metals by heating their chlorides with æthonide of zinc, but the quantities operated upon were too small to give certain results.

I am bound to apologize for sending in my results without an analysis, but the means of doing otherwise are not in my power, and I am in hopes that Dr. Kane will oblige us with more valuable data than I could furnish.

Liverpool, Nov. 28.

XXVI. *Report of some Experiments with Saline Manures containing Nitrogen, conducted on the Manor Farm, Havering-atte-Bower, Essex, in the occupation of Collinson Hall, Esq.* By W. M. F. Chatterley.

Read December 6, 1842.

INDUCED by the prevailing opinion that upon the quantity of Nitrogen contained in some animal and saline manures, depend their fertilizing properties, it was decided to test, by experiment, the relative value of three saline manures containing that element as a constituent, viz. nitrate of potash, nitrate of soda, and sulphate of ammonia, all these salts, from their commercial price, being within the reach of the farmer for agricultural purposes, provided a sufficient amount of profit for the outlay can be shown, and that of course would be preferred by the agriculturist which yields the greatest profit on the prime expenditure.

For the purposes of the experiment a field of WHEAT was chosen, which in the latter end of April, 1842, presented a *thin plant*, the salts were top-dressed over the land by hand, on the 12th of May, in the quantities stated in the table below; the crop was mowed on the 10th of August, and the separate parcels taken from an eighth of an acre, threshed, measured, and weighed under my own inspection on the 24th of August. The results are as follow for the acre:—

No.	Dressing.	Cost per acre.	Produce of Corn & Straw per acre.	Produce of Corn per acre.		Weight of bu. of Corn.	Produce of Straw and Chaff per acre.		Increase of Corn per acre.			Cost of the Increase of Corn per bushel.	Increase of Straw per acre.		Total Increase per cent.	Profit on outlay per cent.
		£. s. d.	lbs.	lbs.	bu.	lbs.	lbs.	tru.	lbs.	b.p.q.		£. s. d.	lbs.	tr		
1	No Manure.....		3700	1413	23⅔	59½	2287	63½								
2	28lbs. of Sulph. Am.	0 5 10	3900	1612½	26⅔	60	2287½	63½	199½	3	1 1	0 1 11½	½	—	14·1	294
3	140lbs. Ditto	1 1 9	4570	1999	32⅔	61½	2571	71½	586	9	0 0	0 2 5	296	3	41·5	212
4	112lbs. Nit. Soda ...	1 4 6	4390	1905	31½	60½	2485	69	468½	7	3 1	0 3 2	198	5½	34·	138
5	112lbs. Nit. Potassa.	1 7 6	4264	1890	31½	60½	2378	66	453½	7	2 1	0 3 8	126	2½	33·5	92

The quantity of nitrogen per cent. in each of the pure salts is as follows:—

	per cent.
Sulphate of Ammonia (crystals) .	18·80
Nitrate of Soda	16·55
Nitrate of Potassa	13·96

This calculation leaves out of the question the adventitious water contained in the salts as they are met with in commerce, and which in nitrate of soda is very considerable, sometimes as much as 10 per cent., and besides, nitrate of potassa usually containing from 2 to 12 per cent. of chloride of sodium, would in each case reduce the per centage of nitrogen. The quantity of solid impurity in the sulphate of ammonia used in these experiments was less than one per cent.

The quantity of gluten in the different samples of wheat, which forms a very considerable item in the determination of the relative value of these manures, was not obtained, in consequence of the error of the foreman, who used the reserved samples for seed; but an approximation may be obtained by comparing the weights of equal bulks, as it is constantly found that the heavier the sample, the more water is absorbed by the flour made therefrom, and consequently the more gluten it contains: by referring to the column of the table which shows the weight of a bushel of each sample, it will be seen, that for the quantities used, sulphate of ammonia (Nos. 2 and 3) is superior to the nitrates of soda or potassa (Nos. 4 and 5).

The object of these experiments having been to approximate the original cost per acre of these manures, rather than their weights, is the reason why equal weights of sulphate of ammonia and nitrates were not used: neither is it believed that the result would at all correspond with the real result of the actual experiment were we to deduct one-fifth from the

product of No. 3; indeed, the product of an acre would not then greatly exceed for 112lbs. of manure that for 26lbs.

It will be observed that the produce of the three manures does not bear a relative proportion to the quantity of nitrogen contained in each, but this gives us no reason for believing that such proportion would not hold good had the quantity of water contained in each been allowed for at the time of dressing.

The attention of the practical agriculturist will probably be attracted to the last column of this table, in which is exhibited the profit on the expenditure in each case; taking the average value of the bushel at seven shillings, and of a truss of straw at ninepence, and calculating chaff as the same value as straw for fodder. The difference between a quarter of a hundred weight and a hundred weight and a quarter of sulphate of ammonia is very remarkable, and, as may be easily perceived, is due to the difference of the value of the produce, the increase in the former instance being wholly in corn, while in the latter it is in both straw and corn, and it is probable that there is some quantity of the manure between these two extremes which would give the largest return relative to the outlay. It is clear however that if a farmer have but 1*l.* to lay out in manure, that the quantity of sulphate of ammonia to be obtained for that sum would give a larger return if spread over four acres of land than if bestowed upon one.

Sulphate of ammonia was also tried as a top-dressing upon a poor *pasture*, at the rate of one cwt. per acre; the operation was performed in the evening after a shower of rain; it was observed on the following day that the clover and some of the grass were withered, indicating that the moisture which remained on the leaves had caused the salt to adhere, and there form too strong a solution; in about a week after this period the grass assumed a greener colour, especially in one part of the field which had been dressed twice over to observe the effect: the crop of hay was not weighed, in consequence of rain coming on at the time of making, but was laid at half a load more to the acre than the undressed portion, and no doubt was entertained that by applying such a dressing earlier (it was not applied till the 12th of May), and in a less droughty season, more time would have been allowed for subsequent growth, and a much larger crop would have been obtained. The after-feed was decidedly improved, and very much preferred by the cattle.

On the same date a quantity of sulphate of ammonia at the same rate, was dressed over a single land in a field of *tares*: the leaves of the plant withered, as in the instance of the pas-

ture above-mentioned, the subsequent produce however was *one-sixth* more than any other land of the field. The oats sown with the tares grew extraordinarily after the application, and it is believed, that if applied earlier in the season to the tares as to the pasture, and during dry weather followed by less drought, the leaves of the plant would not have withered, and the effect would in both cases have been more marked.

On the 21st of May a similar quantity, viz. one cwt. to the acre, of sulphate of ammonia was applied to a field of *clover* in dry weather: in this instance the leaves did not wither, but no increased growth appeared to be the consequence; and a similar result was obtained by the application of nitrate of soda.

To a field of podding peas much infested with slug, the following dressing was applied early in the morning, and by ten o'clock an immense number of the dead insect covered the land:—

Sulphate of Ammonia . .	$7\frac{1}{2}$	cwt. at	17*s.*	0*d.*	6*l.*	7*s.*	6*d.*
Common Salt	2	cwt. at	1	6	0	3	0
Oil Cake, finely powdered	7	cwt. at	6	6	2	5	6

this was sown broadcast, at the rate of $1\frac{1}{4}$ cwt. to the acre (value 14*s.* 6*d.*), and besides saving the plant by the destruction of the insect, seemed in a short time to have converted this crop, from the worst of two others in adjoining fields, into the best of the three, and little or none of the withering effect on the leaves ensued.

It will be observed from the above experiments, that sulphate of ammonia appears to have acted better upon graminaceous than upon leguminous plants; for though the crops of tares and peas seem both to have received considerable benefit from the application, such benefit was by no means in proportion to the effect produced upon wheat or oats; the oats sown with the tares, as has been before observed, growing surprizingly after the application, and exhibiting a marked distinction in their rate of increase.

Sulphate of ammonia, as well as nitrates of soda and potassa, comes under the class of stimulating manures; that is, such manures which, at the same time that they supply the plant with one or more ingredients necessary to the crop, enable it to obtain a larger supply of its usual nourishment from the soil and the atmosphere: hence the quantity of nitrogen itself in the crop from the land to which a nitrogenous manure has been applied, is greater than the sum of the nitrogen from the unmanured portion and the quantity contained in the manure so added; and hence the result of the application of a given quantity of such manure will vary upon different soils, and even

upon the same soil under different conditions, depending upon its capacity to supply the plant with its general nourishment. On account of this stimulant action, care should be taken in the application of these manures, that the quantity used should vary according to the condition of the plant and soil, as too large a quantity on a good plant, with a soil in high condition, would cause the crop to lodge, and a small dressing can always be repeated if found necessary.

From the above experiments and several others, which want of opportunity has prevented from being carried out so fully, but from which as an eye-witness a comparative opinion may be formed, I am led to believe that no cheaper top-dressing than sulphate of ammonia can be applied to wheat or oats on this land, which is generally a heavy clay upon a subsoil of London clay, when the plant requires it, either from its being sickly or thin on the ground, in consequence of the land being somewhat out of condition, whether from unusual wet, bad seed-time, uncongenial spring, or any such-like cause. I should add that equal benefit appears to have been derived from its use upon a light gravelly soil upon a subsoil of gravel, upon the same as the London clay formation.

With respect to the quantity of the salt to be used, it may be best to refer to the practical result of a large and small dressing, as shown in the table above (Nos. 2 and 3), and the previous remarks thereon as to the relative produce of straw and corn in each case, and to add, that although the experiment has not yet been made, there seems reason to believe that a better effect would result from the application of, say one cwt. per acre at three different dressings, than all at once, that is about 37lbs. when the crop of *wheat* makes its spring growth, or when *oats* are about two inches out of the ground; a similar quantity about a month afterwards; and again at the time of the formation of the ear. But a practical difficulty occurs in applying so small a quantity as 37lbs. of any material over an acre of ground: the simplest mode of overcoming this, unless we could use a machine capable of adjustment, similar to what is termed a clover drill, perhaps is to mix the salt with some substance which shall not exert any decomposing action upon it, but so increase its bulk as to enable it to be equally spread over the surface; the best substance, as far as my experience goes, is *common salt* (itself a manure very generally useful), twice the weight of the sulphate being added to make up one cwt., a quantity not difficult to broadcast over an acre: or if preferred, *soot*, which itself contains both sulphate and carbonate of ammonia; or even such a mixture as that before-mentioned used for peas, but then care

must be taken to pulverise the oil-cake sufficiently. A method which has been found to be good is to mix *soot* and *salt* in about equal parts, some weeks previous to the addition of the sulphate of ammonia; the salt condenses moisture from the atmosphere and fixes the carbonaceous particles, and these tend to hold the carbonic acid and ammoniacal gases derived from the atmosphere and decomposing organic matters in the soil, and render them of easy access to the plants. If a very speedy effect be required, the stimulating properties of this dressing may be increased, by setting free a portion of the ammonia by a subsequent *very slight* dressing of hydrate of lime (for obvious reasons this mixture should not be made before the sowing); but as such a dressing is always attended with loss of ammonia, this should never be resorted to unless it is otherwise unavoidable, and if possible when rain may be expected to fall. And this leads me to a remark on the very common practice, in this county particularly, of mixing fermenting farm-yard manure with lime, by which all the ammoniacal salts are decomposed and the ammonia driven off, and a large portion of fertilizing material absolutely lost: it is difficult however to convince the farmer accustomed to this practice, for the immediate benefit which results is considerable; for in the first place the vegetable tissues are broken up, and put in a condition more easily to be converted into carbonic acid, and hence more easily absorbed by plants, and besides its bulk is materially diminished, so that 20 loads of the mixture contains the vegetable matter thus prepared of perhaps 40 of the manure in its ordinary state, and there can be no doubt is more speedily exhausted.

The manures here referred to, and most other saline manures when used as a top-dressing, should be applied when the plant is dry after a shower of rain, or during hazy weather, but not when any continued fall of rain is anticipated; in the first instance it is slowly dissolved by dews, &c., and permeates the soil in every part, and in the latter a considerable portion of its effect is lost as the salt is washed out and carried away in solution by the drains. When the soil is too dry, it remains inactive. It is perhaps supererogative in the present day to insist upon thorough drainage for the effectual action of any manure; it must be clear that unless the soil has been well disintegrated and a free passage exists among its particles, neither moisture, air, nor manure, can thoroughly penetrate, and this condition is effected by drainage alone.

With regard to the use of sulphate of ammonia with the drill and depositing it with the seed: in some experiments

made to determine the propriety of this mode of dressing the land, the result was a thin and bad crop, arising apparently from its having received a check during its early growth, and much of the seed having been killed as soon as germination took place; this may perhaps be accounted for by referring to the withering effect upon the leaves, observed in some of the other experiments, which may be supposed to be much more powerful upon the tender radicle and plumule in the earliest stages of development, while they are provided in the cotyledons of the seed with a mild and bland nourishment suitable for these tender organs, and before they are prepared for procuring or assimilating the stronger aliments fitted only for more mature plants.

Attention has been particularly directed to sulphate of ammonia on account of its low price as compared with other nitrogenous manures, a point upon which the extensive practical application of any manure must chiefly depend. The price paid was seventeen shillings per cwt.; it is prepared at the Gasworks in Brick Lane by a patent process for purifying coal-gas by means of dilute sulphuric acid, and is very free from impurity.

A specimen of manure sold as Daubeny's sulphate of ammonia at 12*s.* the cwt. did not give any traces of ammonia when mixed with caustic lime, but consists almost entirely of sulphate of lime, and is worth no more to the farmer than gypsum which may be obtained at 2*l.* a ton.

This manure is said to be prepared according to the directions of Dr. Daubeny of Oxford, by pouring the ammoniacal liquor of the gasworks upon finely-powdered gypsum: even if it were so, the per centage of sulphate of ammonia to be thus obtained, cannot make its value as compared with pure sulphate of ammonia as 12 to 17; and its name, "Daubeny's Sulphate of Ammonia," unqualified as it is by any explanation of its composition, is liable to lead the agriculturist unable to detect its nature, into serious loss and error.

I may perhaps be permitted to remark, that the nitrogen of coal is the store accumulated by the vegetation of past ages, before man converted it to his use, but now that this inexhaustible source of a material so necessary to increase the quantity of food to be obtained from the present race of plants is opened, it is proper to examine the most advantageous mode of employing it, that so great a boon be neither neglected nor wasted: it should therefore seem to be the duty of all who have it in their power, to confirm or refute the accuracy of such experiments as the above, and if, as I

cannot doubt, they are found to be nearly correct, to promulgate as much as possible the facts, in order that so valuable a material may be speedily appreciated by the British agriculturist.

In conclusion I have to add, that these experiments were not originally commenced with that attention to rigid accuracy which is called for in strictly scientific investigations, for they were in fact intended to serve as illustrations to a course of practical lectures on the application of science to agriculture delivered on the spot, and this may form some excuse for the omission of certain data which could easily have been obtained, but which did not appear necessary until it was decided to calculate and exhibit the results in a tabular form.

XXVII. *On the Sugar of the Eucalyptus.* By James F. W. Johnston, *Esq.*, *M.A.*, *F.R.S.*

Read December 20, 1842.

IN Van Dieman's Land a species of sugar or manna falls in drops or rounded opaque tears from several species of *Eucalyptus*. This is collected in considerable quantity, but it is doubtful still I believe whether it is a natural exudation of the trees from which it falls, or, like the different kinds of honey-dew in our own country, is the consequence of punctures made by insects.

I am indebted for a portion of this manna to Sir W. Jackson Hooker, to whom also I owe the above information regarding its origin. It is soft, slightly yellowish, opaque, is inferior in sweetness to cane-sugar or to ordinary manna, and is in small, rounded, slightly cohering masses. Æther extracts from it only a minute portion of wax, alcohol leaves behind only a small quantity of gum, while water dissolves it without sensible residue.

The aqueous solution crystallizes on evaporation in minute radiating prisms and prismatic needles which form rounded masses having a crystalline structure. It is obtained however from water in distinct crystals with much greater difficulty than from its solution in ordinary alcohol. In boiling alcohol it dissolves in considerable quantity, and is in a great measure precipitated in beautiful white but minute prismatic crystals as the solution cools. It not unfrequently deposits itself also in the form of a white hard and solid crust on the bottom and sides of the bottle into which the hot solution is filtered.

This sugar as it crystallizes from the alcoholic solution has

the same constitution as grape sugar, C_{12} H_{14} O_{14}, or C_{24} H_{28} O_{28}, but it differs from grape-sugar in its appearance, in in its relations to alcohol as above described, in the ease with which it can be obtained in a pure crystallized form, and in its relations to heat.

When suddenly heated at once to 200° or 212°, it melts and loses 5 atoms of water, whereas grape-sugar loses only *four*. But if it be first gradually heated and kept for two or three hours at 180° only, it will part with seven atoms of water *without melting*. In that respect it resembles a salt, which if heated suddenly will melt in its water of crystallization, but by a cautious regulation of the heat may be dried without undergoing fusion. If once melted, this sugar may be kept for several hours at 212° without losing *much* more than the five atoms, and it must be raised to 240° or 250° before it parts with the whole seven, and in every case in which I have made the experiment has even assumed a brown colour, owing to incipient decomposition before the seven atoms have been altogether removed.

When the seven atoms have been driven off by a heat not higher than 200°, the dry powder may be heated to 280°, when it begins to fuse, and may be kept for several hours at 300° without further loss or any change of colour.

After being thus heated the sugar attracts moisture rapidly from the air, and if left over night in a damp room it will assume the form of transparent globules of syrup, which gradually crystallize into colourless radiated masses having the original weight of the portion of sugar experimented upon. We may conclude therefore that the seven atoms are altogether water of crystallization.

When mixed with oxide of lead moistened with water and then gradually dried and heated to 300°, it *appeared* to lose two additional atoms of water without undergoing decomposition; but when exposed to the air on cooling, the mixture rapidly attracts water again from the air. When this mixture after thus heating is boiled with distilled water and thrown upon the filter, a solution of sugar passes through in which hydrosulphurets detect no trace of lead.

The following formulæ exhibit the constitution of this sugar and the loss of weight it undergoes at different temperatures:—

		Loss by experiment, per cent.
Crystallized sugar before or after heating . . .	C_{24} H_{21} O_{21} + 7 HO	
Fused at 212° to 220° .	C_{24} H_{21} O_{21} + 2 HO	11·23

		Loss by experiment, per cent.
Dried without fusion between 180° and 300°	$C_{24}\ H_{21}\ O_{21}$	15·88
Dried at 260° to 300° with oxide of lead . .	$C_{24}\ H_{19}\ Pb_2\ O_{21}$?	20·82?
This again exposed to the air became . . .	$C_{24}\ H_{19}\ Pb_2\ O_{21} + 7\,HO$?	

This sugar, in its relations to alcohol, in the ease and readiness with which it crystallizes from an alcoholic solution, and in the appearance of its crystals, has much resemblance to manna-sugar (Mannite). It is more soluble however in boiling alcohol than mannite, and is therefore obtained in larger quantity on the cooling of the alcohol in which it has been dissolved by the aid of heat. Mannite also, if heated gradually, may be raised to 300° (I do not know how much higher) without either melting or undergoing any loss of weight.

Eucalyptus-sugar gives a precipitate of a slightly brownish tinge with caustic baryta; and a white precipitate is also obtained by mixing it with a solution of ammoniacal trisacetate of lead. This salt of lead I am at present preparing for analysis, and I hope to have the honour of submitting the results to the Society at a future meeting. In the mean time the formulæ presented in this notice must be considered as open to correction.

XXVIII. *On Palladium—Its Extraction, Alloys, &c.* By William John Cock, *Esq.*

Read January 3, 1843.

THIS metal was discovered by Dr. Wollaston in the year 1803, as one of the alloys of native platinum, which for some time after this discovery appears to have been considered the only source of palladium; and as the quantity of the latter metal so alloying the native platinum is very small, it was then considered as a very rare metal: of late years, however, the importation into this country from Brazil of gold dust, alloyed with palladium, has occasioned a much more extensive supply of this metal, as it exists in some specimens of gold dust to the extent of 5 or 6 per cent., and in one instance (that of the gold from the Candonga mine) it constitutes the only alloy of the gold.

The operation of refining is conducted in the following

manner:—The gold dust is fused in charges of about 7 lbs. troy, with its own weight of silver and a certain quantity of nitrate of potash; the effect of this fusion is to remove all earthy matter, and the greater part of the base-metals contained in the gold dust and in the silver melted with it. The fused mixture is cast into ingot moulds, and when cooled, the flux or scoria (containing the oxides of the base metals and the earthy matter, combined with the potash of the nitre) is detached. Two of the bars thus obtained are then remelted in a plumbago crucible, with such an addition of silver as will afford an alloy containing one-fourth its weight of pure gold, and which being first well stirred to insure a complete mixture, is poured through a perforated iron ladle into cold water, and thus very finely granulated; it is then ready for the process of parting. For this purpose about 25 lbs. of the granulated alloy is placed in a porcelain jar, upon a heated sand-bath, and subjected to the action of about 25 lbs. of pure nitric acid, diluted with its own bulk of water: after the action of this quantity of acid, the parting of the gold is very nearly effected; but to remove the last portions of silver, &c., about 9 or 10 lbs. of strong nitric acid is boiled upon the gold for two hours. It is then completely refined, and after being washed with hot water is dried and melted into bars containing 15 lbs. each.

The nitrous acid gas, and the vapour of nitric acid arising during the above process, are conducted by glass pipes (connected with the covers of the jars) into a long stone-ware pipe, one end of which slopes downwards into a receiver for the condensed acid, the other end being inserted into the flue for the purpose of carrying off the uncondensed gas.

The nitrate of silver and palladium obtained as above is carefully decanted into large pans, containing a sufficient quantity of solution of common salt to effect the precipitation (as a chloride) of the whole of the silver, the palladium and copper remaining in solution in the mother liquor, which is drawn off, and when clear is run off, together with the subsequent washings from the chloride of silver, into wooden vessels, and the metallic contents are then separated in the form of a black powder, by precipitation with sheet zinc, assisted by sulphuric acid.

The chloride of silver, when washed clean, is reduced by the addition of granulated zinc washed on the filter with boiling water, dried and melted in plumbago crucibles, without the addition of any flux.

From the black powder obtained as above, the palladium is extracted by resolution in nitric acid and super-saturation with ammonia, by which the oxides of palladium and copper

are first precipitated and then redissolved, while those of iron, lead, &c., remain insoluble. To the clear ammoniacal solution, muriatic acid is then added in excess, which occasions a copious precipitation of the yellow ammonio-chloride of palladium, from which, after sufficiently washing it with cold water and ignition, pure metallic palladium is obtained. The mother liquor and washings contain all the copper and some palladium, which are recovered by precipitation with iron.

Pure palladium is of a greyish-white colour, rather darker than that of platinum; it is both malleable and ductile, though inferior in those qualities to pure platinum; its specific gravity is 11·3, which may be raised by hammering or rolling to 11·8. When perfectly pure it cannot be fused even in small quantities in an ordinary blast furnace, but may be brought into such a state of agglutination as to bear laminating or drawing into wire.

It may be completely fused by means of oxygen gas, and being kept some time fused, is said to burn with the production of brilliant sparks; it is not tarnished by exposure to sulphuretted hydrogen, nor oxidated by the air at the ordinary temperature, or at a bright red heat; but it has the singular property of becoming oxidated by exposure to air at a dull red heat, the surface becoming coloured in the same manner as iron or steel; and by continuing the process cautiously for some time, the metal becomes coated with a brittle crust of oxide of a brown colour; this oxide is, however, reduced by a temperature very little higher than that necessary for its formation; and the surface of the metal regains its original colour upon being heated to a bright red, and cooled out of contact with the air.

It is with difficulty soluble in nitric acid when pure and fused, or in a state of aggregation, but is readily so when alloyed to some extent with silver or copper, and still more so when in the form of the black powder above referred to, in which state it is also soluble with the aid of heat in sulphuric and muriatic acids; but its proper solvent is nitro-muriatic acid, which, if it be not very much alloyed with silver, dissolves it readily.

It is of all the metals that which has the greatest affinity for cyanogen; and by means of cyanide of mercury, it may be separated from all its solutions.

It may be alloyed so as to be malleable with gold, silver and copper, several of its alloys with the two latter metals being of great use in the arts from their hardness and elasticity, and non-liability to rust or tarnish. When added to

gold or copper, it whitens both those metals in a very great degree, about 20 per cent. being sufficient in either case to destroy the colour of those metals.

The uses to which the alloys of palladium have been applied, are for the points of pencil-cases, for lancets for vaccination, for the graduated scales of instruments, as a substitute for gold in dental surgery, or for any purpose where strength and elasticity, or the property of not tarnishing, is required.

XXIX. *On the Formation of Fat in the Animal Body.* By Justus Liebig, *Ph.D., M.D., F.R.S., &c.*

Read January 3, 1843.

[Translated from the German original by Mr. E. F. Teschemacher.]

IN my published work on 'Organic Chemistry, in its application to Physiology and Pathology,' I have endeavoured to explain the nutrition of the human and animal organism, according to the present state of organic chemistry. I have pointed out the relation between the nitrogenous food and the nitrogenous constituents of animal bodies, and have considered the non-nitrogenous constituents of the food as the means of the formation of the non-nitrogenous constituents of animals.

The circumstance, that the large class of carnivorous animals do not take any sugar, starch, or gum in their food, leads of itself to the opinion that these substances are not required for proper nourishment, namely, for the formation of blood; and as it appears from the analysis of plants containing nitrogen, that they possess a similar composition to the substances of the blood, it follows also that in the bodies of herbivorous and graminivorous animals, the carbon of the sugar, gum and starch cannot be applied to the formation of the blood. The nitrogen of the nitrogenous ingredients of the food is therefore in a state of combination, in which the elements necessary for the production of the albumen are already present both in number and relative proportions; in the food of the graminivorous animals, we know after all of no other compound, which can supply nitrogen to starch, sugar, or gum, for the production of albumen.

As sugar, gum and starch, in their normal state, disappear in the vital processes of graminivorous animals, and as they are given out of their bodies as carbonic acid and water, it

follows from such a conversion that they serve by means of the respiration for the production of animal heat.

The disappearance of fat in animals in consequence of disease, or of an increased absorption of oxygen, and its being given out in the form of carbonic acid and water, is a proof that that non-nitrogenous body is converted to the same use as sugar, gum, or starch in animal bodies, and for want of other non-nitrogenous food is applied to the respiration.

The further consideration, that the flesh of the carnivorous, which of all animals eat most fat, contains no fat, and is not eatable; that the fat in the bodies of graminivorous animals increases when the process of respiration, and with it the absorption of oxygen diminishes, through a want of exercise or an increase of temperature, leads to the conclusion that the fat has its origin in the non-nitrogenous food, the carbon remaining in the body in the form of fat when there is a deficiency of the necessary quantity of oxygen to convert it into carbonic acid.

Supported by the example of what certainly takes place in the processes of fermentation and putrefaction, in which sugar and starch, by giving out oxygen or carbonic acid, form new combinations, which, like æther and fusel oil, more resemble fat in their properties than any other known compounds, I have endeavoured to trace out the formation of fat, on the supposition that the carbon of non-azotized substances remains in the animal body in the form of fat.

According to my statement, the fat consequently originates from the non-nitrogenous constituents of the food: let us suppose from sugar, then this must have undergone a chemical change in conformity with my proposition.

The formation of wax from honey which contains none, in the body of the bee, of which, from the experiments of M. Grundlach of Cassel, there can be no doubt, appears to remove every objection to the possibility of such an action taking place.

I never had the least idea of defending in my book the opinion, or even of expressing it, that the fat which was taken in the food of animals did not contribute to increase the quantity of fat in their bodies; but I was not aware of any supply of butter in the grass which is daily consumed by cows, or of tallow, of lard, or goose-fat in potatoes, barley and oats; in the analyses of these substances as at present given, they contain only waxy substances, and that in such a small quantity that I consider the formation of fat could not be attributed to it.

These ideas concerning the origin of fat in animal bodies took a new direction from a note which M. Dumas appended in the *Annales de Chimie* (new Series, vol. iv. p. 208) to my treatise on the nitrogenous food of the vegetable kingdom; in this note M. Dumas says,—"M. Liebig is of opinion that graminivorous animals *produce* fat out of sugar and starch, while MM. Dumas and Boussingault consider it as a fixed rule, that animals, of whatever kind, produce neither fat nor any other alimentary substance; that they receive from the vegetable kingdom all their aliments, whether it be sugar, starch, or fat.

"Were the proposition of M. Liebig founded upon fact, the general formula of chemical equivalents of both kingdoms, as defined by MM. Dumas and Boussingault, would be false. But the commission on gelatine has dispelled all doubt, that the animals which eat fat are the only ones in which fat is found to accumulate in the tissues."

The origin of fatty compounds in animal bodies has, through this note, become a question of dispute.

As far as regards myself, I have neither time nor inclination to engage in it; the object of my observations was to leave no doubt of the physiological importance of the fat of animal bodies, as regards the process of respiration. In this view MM. Dumas and Boussingault agree with me.

I think it now right to explain the reasons which induced me to consider that little or no increase of fat in animal bodies was to be ascribed to the ingredients of the food containing fat, consumed by graminivorous animals.

The food which, according to the experience of physicians, has a decided influence on the formation of fat in animal bodies, is that which is richest in starch, sugar, and other substances of a similar constitution.

Rice, Indian corn, beans, peas, linseed, potatoes, beet are used in husbandry in large quantity with great effect for fattening, that is, for the increase of flesh and fat. In Bavaria beer is used as a stimulating food for the increase of fat.

Whether much or little importance may be ascribed to the universal experience of husbandry, it is certain that animals which are fed upon these different substances, under certain conditions (abundance of food, little exercise, high temperature, &c.), after some time become much fatter than before. This fat proceeds from the food. Rice, beans and peas have been carefully analysed by various chemists. Braconnot found in Carolina rice 0·13 per cent. of oil, in Piedmont rice 0·25 per cent.; Vogel found in rice 1·05 per cent.

According to these analyses, the organism received from 1000 lbs. of Carolina rice 1·3 lb. or 2·5 lbs., or according to Vogel 10½ lbs. of fat.

Peas contain, according to Braconnot, 1·20 of a substance soluble in æther, which he calls leafgreen (chlorophyll). The bean of the *Phaseolus vulgaris*, according to the same chemist, contains 0·70 of fat soluble in æther. Fresenius obtained from peas 2·1 per cent. of a substance soluble in æther, from linseed 1·3 per cent.

For every 1000 lbs. of peas or beans the organism receives, according to Braconnot 12 lbs., according to Fresenius 21 lbs. of fat, and from as many beans only 7 lbs. of fat.

Beer, as far as I am aware of, contains no fat: Fresenius obtained from the pulp of the beet-root 0·67 per cent. of a substance soluble in æther.

According to further direct examinations made in our laboratory, 1000 parts of dried potatoes gave 3·05 parts of a substance soluble in æther. This substance possessed all the properties of resin or wax; we will, however, assume that potatoes contain $\frac{3}{1000}$ of their weight of fat. Three one-year-old pigs, fattened with 1000 lbs. peas and 6825 lbs. potatoes fresh boiled, which are equal to 1638 lbs. of dried potatoes, increased in weight in thirteen weeks from 80 lbs. to 90 lbs. each. A fully fattened pig averages in weight from 160 lbs. to 170 lbs., and after killing the fat weighs from 50 lbs. to 55 lbs. The three pigs have consumed 21 lbs. of fat, contained in the 1000 lbs. peas, and 6 lbs. in the 1638 lbs. of potatoes, together therefore 27 lbs. Their bodies, however, contained from 150 lbs. to 165 lbs. of fat. There is an increase of from 123 lbs. to 135 lbs. more fat than the food contained. A pig one year old weighs from 75 lbs. to 80 lbs.; suppose it to contain 18 lbs. of fat, there still remains, leaving entirely out of question the matters soluble in æther contained in the excrements, 69 lbs. to 74 lbs. of fat*; the production of which

* M. Vogt, a butcher at Giessen, in answer to some questions of mine, gave me the following as the result of his experience, which has been confirmed by other intelligent persons:—A restless pig is not adapted for fattening, and however great the supply of food it will not grow fat. Pigs which are fit for fattening must be of a quiet nature; after eating they must sleep, and after sleeping must be ready to eat again. When a pig is a year old it weighs from 75 lbs. to 80 lbs., and if the fat is intended to be used as lard, it must be fed daily for thirteen weeks with 20 lbs. to 25 lbs. of boiled potatoes, and about a measure of peas (2 litr.); towards the end of the time the food may be somewhat diminished. A pig so fattened weighs from 160 lbs. to 170 lbs., and contains of fat and lard, taken altogether, from 50 lbs. to 55 lbs. A pig of a year old has a lard membrane under which the lard is secreted, but at that age it does not contain lard.

in the organization cannot be doubted, and whose formation remains to be accounted for.

M. Boussingault's examinations concerning the influence of food on the quantity and composition of the milk of the cow, furnish other more important grounds for the opinion that animals produce fat out of certain food, which is neither fat itself, nor contains fat (*Annales de Chim. et de Phys.* t. lxxi. p. 65).

M. Boussingault's experiments correspond with universal experience, and I believe are to be relied upon; it is, therefore, the more inconceivable to me that he has placed himself by the side of those who support the opposite opinion.

A cow was fed at Bechelbrunn during eleven days upon daily rations of 38 kilogrammes of potatoes, and therefore in eleven days upon 418 kil. Also 3·75 kil. chopped straw; in eleven days, 41·25 kil. In these eleven days she gave 54·61 litres of milk, which contained 2284 gram. butter. As 418 kil. of fresh potatoes are equal to 96·97 kil. of dry potatoes (potatoes contain, according to M. Boussingault, 76·8 water and 23·2 solid matter, *Annales de Chim. et de Phys.* 1838. p. 408); further, as 1000 gram. potatoes contain only 3·05 gram. of soluble matter, and the straw, according to experiments made here, contains only 0·832 per cent. of a substance soluble in æther (a crystalline wax), the cow had, therefore, in eleven days consumed 291 + 343 gram. = 634 gram. of substance, soluble in æther. There was contained in this milk however 2284 gram. of fat.

In another case, in a trial carried on in winter, the daily rations of the cow was for a long time 15 kil. of potatoes and $7\frac{1}{2}$ kil. of hay. The quantity of milk amounted in six days to 64·92 litres. These 64·92 litres of milk contained 3116 gram. of butter. In six days the cow consumed 90 kil. of fresh potatoes, equal to 19·88 of dried; in the same time 45 kil. of hay were consumed. Suppose that the 19·88 kil. of potatoes supplied to the cow contained 60 gram. of fat, the other 3056 gram. of butter must have originated from the 45 kil. of hay. According to this, hay must contain nearly 7 per cent. of fat. This is easily ascertained by experiment.

From hay of the best quality, in the state in which it is consumed by the cows, 1·56 per cent. of a substance soluble in æther was obtained in the Giessen laboratory. Taking the hay to contain 1·56 per cent. of butter, the 45 kil. of hay could supply the cow with only 691 gram., there remains, therefore, to discover whence the other 2365 gram. of butter originated which M. Boussingault found in the milk.

In a note which M. Dumas has appended to a communication of M. Romanet's (*Comptes Rendus de l'Acad. des Sciences*, 24 Oct.), the following remarks are made:—

"Hay contains in the state in which it is consumed by the cow, nearly 2 per cent. of fatty matter. We will show (MM. Dumas and Payen) that the ox which is fattened and the milch cow furnish a *smaller* quantity of fatty material than the fodder contains. As regards the milch cow in particular, the butter in the milk corresponds very nearly with the quantity of fatty material contained in its food; at least as far as in that of the food we have yet studied, namely hay and Indian corn, which last the cow does not usually obtain as food."

After the foregoing facts, which I could considerably multiply, it will be very difficult for MM. Dumas and Payen to prove that the cow, for instance, furnishes from the fatty matter contained in the food only the corresponding quantity of butter. The proof of the supposition, besides, that animals receive the fat in their food in the same state as it is found in their bodies, is impossible. Nothing is easier to decide than the question whether or not the butter which the cow produces, is contained as butter in the hay.

Hay gives after exhaustion by æther a green solution, and on evaporation a green residue, with a strong agreeable smell of hay, which possesses no properties characteristic of fatty substances. This green residue consists of various substances, of which one is of a waxy or resinous nature, known under the name of chlorophyll; another ingredient of the same crystallises from a concentrated æthereal solution in minute laminæ, and is the crystalline wax which Proust obtained from plums and cherries, from the leaves of cabbages, from a species of *Iris*, and from grasses, and which is probably identical with the wax that Avequin collected in such large quantities from the leaves of the sugar-cane. M. Dumas has analysed this substance, and found it to differ both in composition and properties from any of the known fats; in consequence of which he felt justified in giving the name cerosine to this substance.

M. Fresenius obtained by means of æther from straw, and M. Jägle, of Strasburg, from the fresh plant, *Fumaria officinalis* (in the Giessen laboratory), by means of alcohol, a crystalline wax, very similar to cerosine. The occurrence of wax in the vegetable kingdom is very extensive, generally accompanied by chlorophyll.

Margaric or stearic acid, the principal ingredient of the fat of animals, is neither found in the seeds of corn, nor in herbs nor in roots which serve as food. It is evident that if the

ingredients of the food soluble in æther are convertible into fat, margarine and stearine must be formed out of wax or chlorophyll.

As far as our experience goes, the chlorophyll of the food taken in a green state is given out from the body unchanged; even in man the excrements retain the colour of the green vegetables consumed. It is also considered that the wax does not experience any change in the organism. All doubt may be removed by the simplest experiments; it may be shown that the excrements of the cow contain as much of the substances soluble in æther as has been consumed in the food. The excrements of a cow which was fed upon potatoes and grass were dried and exhausted by æther; a green solution was obtained, somewhat darker in colour than that given by hay, which upon concentration owed its consistency to a white crystalline waxy substance, which was surrounded by a dark green mother liquor. Upon further evaporation it gave out an unpleasant smell, and left when dried at 100° C., 3·119 per cent. of the weight of the excrements of fat and similar substances.

As M. Boussingault has found that the dried solid excrements (*Annal. de Chim. et de Phys.* t. lxxi. p. 322) amount to four-tenths of the weight of the dried fodder, it is evident that these excrements contain very nearly the same quantity of fatty substances as the food consumed.

7½ kilogr. of hay contain (at 1·56 per cent.) 116 gram. of fat. The 15 kilogr. of potatoes contain further 10 gram. of fat. In the whole, therefore, 126 gram. of fat.

The solid daily excrements weigh 4000 gram.; they contain (at 3·119 per cent.) 124·76 gram. of fat. A cow which produces in six days 3116 gram. of butter, consumes in its food during the same period 756 gram. of substances soluble in æther, and gives off in her excrements 747·56 gram. of substances of the same nature and properties; it must therefore follow, that in the production of 6¼ lbs. of butter in the milk, these ingredients of the food can have no share.

I consider I have now demonstrated that the fat which accumulates in the bodies of animals during the fattening process, and that the butter daily produced in the milk, do not originate from the wax or chlorophyll of the food, but from the other ingredients of it. I think I should be giving myself unnecessary trouble to look after facts to correct M. Dumas's peculiar opinion, because upon further consideration it is of a nature to correct itself.

It is similar to the idea of M. Payen, that the oil of potato spirit (fusel oil) is ready formed and contained in potatoes. But since it has been found that the last syrup

arising from the preparation of beet-root sugar produces in the distillation of brandy a considerable quantity of fusel oil, no one will doubt its formation during the process of fermentation.

The opinion of M. Dumas is a necessary consequence of the exclusive hypothesis, that animals produce in their organism no substances serving as food (note quoted above), but that they receive all sustenance, whether sugar, starch, or fat, from the vegetable kingdom.

I agree perfectly in opinion with M. Dumas in relation to the substances which serve for the formation of blood; but differ from him in considering it as fully proved, as far as observation extends, that wax is formed in the body of the bee, and fat in the stall-fed cow.

In regard to the principle of M. Dumas, that the organism of an animal is not able to produce any substance serving as food, it is equivalent to saying that the organism produces nothing, but only transforms it; that no combination takes place in its body, when the materials are not present by means of which the metamorphosis originates. Thus the formation of sugar of milk in the bodies of carnivorous animals cannot take place, for dog's milk, according to Simon, contains no sugar of milk. Thus also fat cannot be produced in their organism; because, besides fat, they do not consume any non-nitrogenous food. But starch, gum and sugar contain, even with their large quantity of oxygen, all the ingredients of fatty bodies; and the formation of butter in the body of the cow, and of wax in that of the bee, leave hardly any doubt that sugar, starch, gum, or pectine, furnish the carbon for the *formation* of the butter or of the wax.

It is further certain that the brain (Fremy), the nerves, the blood (Lecanu), the fæces, and the yellow of the egg (Chevreul), contain a substance in considerable quantity with a far smaller proportion of oxygen than the known fatty acids, a substance which hitherto has not been found in the food of graminivorous animals. The formation of cholesterine from fat cannot be supposed without a separation of oxygen or of carbonic acid and water; it must be derived from a substance far richer in oxygen in consequence of a process of decomposition or metamorphosis, which, applied to the case of starch or sugar, explains their conversion into fat in the simplest manner.

In the before-mentioned note to the observations of M. Romanet, M. Dumas attempts, from the facts quoted in the preface to my Pathology, to weaken the conclusion to which I had arrived concerning the formation of fat in the animal

body. These facts concern the quantity of fat in a goose fed upon Indian corn (maize), which corn I have alleged not to contain a thousandth part of fat or fatty substance. The experiments of M. Liebig, says M. Donné in the *Journal des Débats*, are throughout inexact and false, as MM. Dumas and Boussingault have obtained 9 per cent. of a yellow oil from Indian corn, which M. Dumas had the honour to exhibit to the Academy.

It must be evident to every unprejudiced person, that the fact mentioned in the preface has no necessary connexion with the discussion, concerning the production of fat, in the work itself, or in the appendix; it is not employed in the argument. While writing the preface, a friend of mine communicated to me the result of fattening geese with Indian corn. I found in the *Jour. de Chim. Médicale*, i. p. 353, an analysis of maize by Lespes, in which no trace of a fatty substance is mentioned. I further found by an examination by Gorham, in the 'Quarterly Journ. of Science,' xi. p. 205, that maize contained a particular substance, which he called zein, which was extracted by alcohol and could not be fat, as, on the authority of Gorham, this zein was not miscible with fat oils. Gorham does not mention any fat oil.

Therefore, according to every fact of which I was aware, maize contained neither fat nor any substance similar to fat. I had not myself at that time entered into any examination of it. The results obtained by MM. Dumas and Payen induced me, however, to undertake an examination of Indian corn, which was grown in my garden.

67 gram. of maize were exhausted by æther. The æther left behind, on evaporation on the waterbath, 2·849 gr. of a thick yellow oil.

The weight of this oil amounted to 4·25 per cent. of the seed. The difference in this experiment from that of MM. Dumas and Payen is very great; 9 per cent. is so much that this seed might be used with advantage in the manufacture of oil. I consequently altered the mode of examination by a proceeding which insured a perfect extraction. The seeds were treated with dilute sulphuric acid kept at nearly a boiling heat until they had almost disappeared. The residue was washed, dried and exhausted by æther. 77 grm. produced in this manner 3·594 grm. of a substance soluble in æther. Maize grown in the fruitful fields of Giessen, therefore, does not contain more than 4·67 per cent. I found since also an analysis by Bizio (*Brugnatelli Giornale*, t. xv. pp. 127, 180) which gives for Italian maize 1·475 per cent of fat oil.

Maize belongs to those seeds which produce a decidedly

favourable influence on the formation of fat; some maize contains no fat (Lespes, Gorham), some contains above 4 per cent. of oil, and other maize contains 9 per cent. of fatty oil. According to each individual's view, arguments may be drawn from these observations favourable or unfavourable to the formation of fat in the animal body; but as the analysis of the excrements of the geese was not made, they cannot be taken into account.

The fatty oil obtained in the Giessen laboratory from the seeds of the maize, completely dissolved in an alkaline carbonate and formed a perfect soap; it consisted of a fatty acid, which probably is formed by the influence of the air on the fat contained in the seed on its becoming rancid.

According to the analysis of Dr. Fresenius, this oil consists in 100 parts of—

Carbon	79·68
Hydrogen	11·53
Oxygen	8·79

and possesses, therefore, a composition similar to known fats.

I consider it certain, that the fat which animals take in their food contributes to increase the quantity of fat in their bodies. We have of this certain and decided proof, in the pathological treatment of persons who daily take a considerable quantity of cod-liver oil.

I further consider it probable that oily fat may pass into crystallized fatty acids; and Wöhler's observation, that fusel oil from corn contains a considerable quantity of margaric acid, finds a satisfactory solution by the experiments of M. Mulder, which make the conversion of ænanthic acid into margaric acid probable.

In the Giessen laboratory the observation was made some years ago, that the oleic acid, in the state in which it is obtained from stearic acid manufactories, produces upon rapid distillation more than the half of a fluid product which on cooling becomes as hard as tallow, and upon expression produces 35 per cent. of margaric acid.

These experiments, which are well worth a closer investigation, render it not improbable that hard tallow might be formed out of liquid crystallizable oil.

Whether similar processes take place in animals, in relation to the formation of many of their compounds, to those that take place in plants, is hardly to be doubted.

The observation by Wöhler of the giving out of oxygen by the infusoria, which led him to put the question, whether the nourishment of these creatures was not dependent upon

a similar decomposing process to that of plants, might by accurate examination be soon brought to a decision.

XXX. *On the Changes in Composition of the Milk of a Cow, according to its Exercise and Food.* By Lyon Playfair, *Ph.D., Honorary Member of the Royal Agricultural Society of England.*

Read 17th January, 1843.

As the principal object of this paper is to draw the attention of practical men to the conditions which effect a change in their dairy produce, it has been written in a more elementary form than would have been done, had its purpose merely been to communicate facts to scientific chemists. The object of the Chemical Society is to examine the applications of chemistry to practice, as well as to assist in the advancement of the abstract science. Many difficulties occur in the pursuits of a dairy farmer, which render his occupation precarious. Such difficulties arise entirely from an ignorance of the scientific relations of the practice in which he is engaged. I have endeavoured in the following paper to point out the causes which so often effect changes in the nature of his produce.

Boussingault and Lebel* instituted some experiments, with the view of proving that the composition of milk remains constant, when the food given to the cow contains the same amount of nitrogen: and their analyses established this fact, as far as regarded the casein in the milk; although its other ingredients varied very considerably, according to the nature of the food. The mean of eight analyses described in the first part of their memoir, gives the following composition for the milk of a cow:—

Casein	3·2
Butter	4·1
Sugar	5·1
Ashes	0·2
Water	87·4

The method employed by these chemists in their analyses did not differ from that used by Peligot in his examination of the milk of the ass†.

It consisted in treating the solid residue of a known weight of milk with æther, and afterwards with water. The loss in weight, after washing with æther, was estimated as butter,

* *Ann. de Chim. et de Phys.* lxxi. 65. † *Ibid.* lxii. 432.

while that experienced by a similar treatment with water indicated the quantity of sugar; the dried insoluble residue being casein. The latter was incinerated, in order to obtain the ashes of the milk.

There is an error in this method of analysis, which seems to have escaped the attention of Boussingault and Lebel. It consists in the neglect of the inorganic matters dissolved by the water. In washing with water the mixture of casein and sugar, all the soluble salts of the milk are dissolved. The insoluble salts remain in the residual casein, and these alone were obtained by its incineration, whilst those dissolved by the water were neglected. Consequently, in the analyses of Boussingault, the quantity of sugar in the milk is always too high, and that of the inorganic ingredients too low.

The method of analysis employed in this paper was, with a few modifications, the same as the above. A weighed portion of milk, to which a few drops of acetic acid had previously been added, was evaporated to dryness at the heat of boiling water (212°). The solid residue was digested with æther, thrown upon a weighed filter, and well washed with hot æther. The mixture of sugar and casein remaining on the filter being again dried at 212°, indicated by its loss in weight the quantity of butter dissolved by the æther. The æthereal solution itself was evaporated to dryness, and consisted of butter with colouring matter, more or less intense, according to the character of the food. The mixture of casein and sugar was washed with hot water, and the casein remaining on the filter, after being dried at 212°, was weighed, then incinerated, its ashes determined and deducted from the weight of the casein. The solution of sugar, being evaporated by a heat of 212°, yielded a residue consisting of sugar of milk and of the soluble salts of the milk. This residue, after being weighed, was incinerated and its ashes determined. These, deducted from the weight of the residue, yielded the amount of sugar, and added to the ashes of the casein, indicated the total amount of inorganic ingredients in the milk. The ashes of the filter were of course subtracted.

The cow which was made the subject of the following experiments is of the breed of short horns. I am not aware of the number of days since she was delivered of her last calf. When the experiments were instituted, she was in good milking condition. In order to estimate the average amount of her milk, I measured it for several days previous to the experiments. During this time she subsisted upon aftergrass; the meadow being about half a mile distant from the cow-house.

	Morning's milk.	Evening's milk.
October 5	5 quarts	4½ quarts
... 6	5 ...	4 ...
... 7	4½ ...	5 ...
... 8	5 ...	4 ...
... 9	5¼ ...	4 ...

The weather was fine for the period of the year; but the nights being rather cold, on the evening of the 7th I directed that the cow should be driven to the house, and remain there during the night. In the morning it was put out to grass, but brought back in the evening. On the evening of the 9th I commenced the analyses, and followed them up in consecutive days. In every case the specimen of milk analysed was taken from the milk-pail, after the cow had been thoroughly milked, and the milk well stirred. This precaution was necessary, because the separation of the cream from the milk takes place in part in the udder of the cow. Hence the milk last drawn from the udder contains much more cream than that first obtained*.

1st day. The cow, fed in the meadow upon after-grass during the day, was driven home to the cow-house in the evening. The milk then obtained amounted to four quarts. A portion of this was subjected to analysis.

Specific gravity of milk, 1034.

11·128 grammes of milk gave—		In 100 parts.
Casein	·611	5·4
Butter	·404	3·7
Sugar of milk . .	·429	3·8
Ashes	·068	0·6
Water	9·616	86·5
	11·128	100·0

During the day the cow had considerable exercise. Before being milked, it had half a mile to walk from the meadow. The nourishment in after-grass being small compared with fresh grass, the animal had to eat a greater quantity than it otherwise might have done, and consequently had to traverse more ground in order to procure it. The exercise which it thus received, by increasing the number of its respirations, must have occasioned a greater supply of oxygen to the system. This oxygen, as we shall afterwards show, unites with the butter and consumes it; consequently less butter is

* Schübler says that the milk last drawn contains three times as much cream as that first procured.

Dr. Anderson (Dickson's Practical Agriculture, vol. ii. p. 999) found the cream in the last cup of milk drawn from the udder, compared with that of the first cup, in the proportion of 16 to 1.

contained in the milk of the cow than would have been the case had its pasture been rich grass.

But, after being removed into the shed, less oxygen was respired, and the warmth of the house was equivalent to a certain amount of unazotised food*. The animal received nothing to eat during the night, and therefore the milk of the morning must have been derived from the after-grass consumed during the day. This milk measured four and a half quarts.

Specific gravity, 1032.

15·280 grammes yielded—		In 100 parts.
Casein	0·610	3·9
Butter	0·864	5·6
Sugar of milk. .	0·468	3·0
Ashes	0·091	0·5
Water	13·247	87·0
	15·280	100·0

The butter, as we might have expected, is in larger proportion than in the previous analysis. The amount of casein is smaller.

We shall defer the consideration of the causes which produce a variation in the quantities of the latter constituent.

2nd day. The object of this day's experiment was to discover whether an increase of butter would be procured by feeding the cow with after-grass in the stall. It refused, however, to eat this food, and being removed from its companions, struggled for several hours to regain its liberty. To render it tranquil, a companion was introduced into the same stall, and it was then induced to consume 28 lbs. of good hay and $2\frac{1}{2}$ lbs. of oatmeal. The milk of the evening measured $3\frac{1}{2}$ quarts.

Specific gravity, 1031.

22·684 grammes yielded—		In 100 parts.
Casein . . .	1·124	4·9
Butter . . .	1·150	5·1
Sugar . . .	0·867	3·8
Ashes . . .	0·137	0·5
Water . . .	19·406	85·7
	22·684	100·0

The milk of the morning amounted to 4 quarts; but, owing to an accident, was not analysed.

3rd day.—A. The cow was kept in the shed, and consumed 28 lbs. of hay, $2\frac{1}{2}$ lbs. of oatmeal, and 8 lbs. of bean-flour. The milk of the evening amounted to 4 quarts = 10·34 lbs.

* In this paper we take for granted that the leading features of Liebig's 'Animal Physiology' are acknowledged as true.

Specific gravity, 1034.

23·160 grammes gave—		In 100 parts.
Casein . . .	1·262	5·4
Butter . . .	0·905	3·9
Sugar of milk	1·112	4·8
Ashes . . .	0·136	0·5
Water . . .	19·745	85·4
	23·160	100·0

B. The quantity of milk obtained in the morning amounted to $4\frac{1}{2}$ quarts = 11·61 lbs.

Specific gravity, 1032.

19·445 grammes of milk gave—		In 100 parts.
Casein . . .	0·758	3·9
Butter . . .	0·888	4·6
Sugar . . .	0·877	4·5
Ashes . . .	0·129	0·7
Water . . .	16·793	86·3
	19·445	100·0

4th day.—A. The cow, kept in the stall as before, received this day 24 lbs. of potatoes (steamed), 14 lbs. of hay, and 8 lbs. of bean-flour. She gave in the evening 5 quarts of milk = 12·9 lbs.

Specific gravity, 1033.

17·820 grammes of milk gave—		In 100 parts.
Casein . . .	0·707	3·9
Butter . . .	1·190	6·7
Sugar of milk	0·815	4·6
Ashes . . .	0·104	0·6
Water . . .	15·004	84·2
	17·820	100·0

B. The milk of the morning amounted to 4 quarts = 10·32 lbs.

Specific gravity, 1032.

19·641 grammes of milk yielded—		In 100 parts.
Casein . . .	0·535	2·7
Butter . . .	0·978	4·9
Sugar of milk	0·991	5·0
Ashes . . .	0·116	0·5
Water . . .	17·021	86·9
	19·641	100·0

5th day.—A. The cow, kept as before, consumed 14 lbs. of hay and 30 lbs. of potatoes (steamed). She gave in the evening $5\frac{1}{8}$ quarts of milk = 13·18 lbs.

Specific gravity, 1030.

18·141 grammes of milk yielded—		In 100 parts.
Casein . . .	0·716	3·9
Butter . . .	0·845	4·6
Sugar of milk	0·713	3·9
Ashes . . .	0·099	0·5
Water . . .	15·768	87·1
	18·141	100·0

B. The milk of the morning amounted to $4\frac{3}{4}$ quarts = 12·20 lbs.

Specific gravity, 1030.

16·740 grammes yielded—		In 100 parts.
Casein . . .	0·600	3·5
Butter . . .	0·835	4·9
Sugar . . .	0·648	3·8
Ashes . . .	0·082	0·5
Water . . .	14·575	87·3
	16·740	100·0

Before proceeding to the consideration of these experiments, it is necessary that we should examine the composition of the various kinds of food given to the cow. The cow received, during the course of the experiments, grass, oatmeal, hay, beans, and potatoes. The following analysis exhibits the composition of these various substances.

	Hay. Boussingault.	Oats. Boussingault.	Beans. Playfair.	Potatoes. Boussingault.
Carbon . .	38·47	41·57	38·24	12·30
Hydrogen .	4·20	5·25	5·84	1·74
Oxygen . .	32·51	30·10	33·10	12·04
Nitrogen .	1·26	1·80	5·00	0·32
Ashes . .	7·56	3·28	3·71	1·40
Water . .	16·00	18·00	14·11	72·20

In a specimen of beans analysed by Boussingault, only 4 per cent. of nitrogen was found. But in the bean-flour, which I used in the experiments, there was as much as 5 per cent. It is obvious that if we multiply the quantity of nitrogen by $6\frac{1}{3}$, the product will be the amount of casein or albumen in the various kinds of food; and further, by deducting this, together with the water and ashes, the remainder must indicate the quantity of unazotised matter.

	Albumen or casein.	Unazotised matter.
Hay . .	7·81	68·63
Oats . .	11·16	67·56
Beans . .	31·00	51·18
Potatoes .	1·98	24·42

Finally, according to Liebig, good hay contains 1·56 per cent. of a fatty or waxy substance. Braconnot found 0·70 per

cent. of a similar substance in beans. Vogel found 2 per cent. in oats, and Liebig 0·3 per cent. in potatoes.

Dumas, in an announcement to the French Academy, has lately advanced the theory, that the fat of animals is wholly derived from the fatty matter contained in their food. This opinion has been very ably combated by Liebig, who refers to an analysis of milk executed by Boussingault, and shows that much more butter was contained in it than could be accounted for by the fat in the food taken. As the theory of the formation of fat is of the first importance in the practice of dairy farming, we will shortly examine Dumas's theory with reference to the preceding experiments.

1. On the 2nd day the cow received 28 lbs. of hay, which contains 0·436 lb. of fat and $2\frac{1}{2}$ lbs. of oatmeal, containing 0·050 lb. of the same constituent. The cow produced (calculating according to its specific gravity) about 19 lbs. of milk, in which was 0·969 lb. of butter. But the food altogether contained only 0·486 lb. of fat, so that 0·483 lb. of butter must have been produced from other sources.

2. The food received by the cow on the 3rd day consisted of 28 lbs. of hay, $2\frac{1}{2}$ lbs. of oatmeal, and 8 lbs. of bean-flour.

28 lbs. of hay contain . . .	0·436 lb. of fat.
$2\frac{1}{2}$ lbs. of oatmeal contain .	0·050 lb. of fat.
8 lbs. of beans contain . .	0·056 lb. of fat.
In the food	0·542 lb. of fat.

The milk of the evening amounted to 10·34 lbs., and contained 0·4 lb. of butter; that of the morning to 11·61 lbs., and contained 0·5 lb. of butter. The butter in the milk amounted, therefore, to 0·9 lb., of which only 0·542 lb. could possibly have been furnished by the food, assuming that the fat in the food could be converted into butter.

3. The cow received on the 4th day 14 lbs. of hay, 8 lbs. of beans, and 24 lbs. of potatoes.

14 lbs. of hay contain . . .	0·218 lb. of fat.
8 lbs. of beans contain . .	0·056 lb. of fat.
24 lbs. of potatoes contain .	0·072 lb. of fat.
	0·346

The evening's milk amounted to 12·9 lbs., and contained 0·86 lb. of butter; that of the morning to 10·32 lbs., and contained 0·50 lb. The cow, therefore, furnished during the day 1·36 lb. of butter. The fat in the food amounted only to 0·346 lb., and therefore 1·064 lb. must have been received from other sources.

4. On the 5th day the cow received 14 lbs. of hay and 30 lbs. of potatoes.

14 lbs. of hay contain . . .	0·218 lb. of fat.
30 lbs. of potatoes contain .	0·090 lb. of fat.
	0·308

The milk of the evening amounted to 15·18 lbs., and contained 0·606 lb. of butter; that of the morning to 12·20 lbs., containing 0·597 lb. of butter. The cow, therefore, furnished 1·203 lb. of butter. The fat in the food amounted only to 0·308 lb. Hence 0·895 lb. of butter must have been produced from other sources.

From these calculations it must be obvious, that the butter in the milk could not have arisen solely from the fat contained in the food. Hence it must have been produced by a separation of oxygen from the elements of the unazotised ingredients of the food of the animal, in the manner pointed out by Liebig.

We remark striking variations in the quantity of butter in the preceding analysis, and a similar result occurred in the experiments of Boussingault. In the milk of the first day there is a small amount of butter. The cow had been exposed in the field during the day, and hence required a greater quantity of unazotised food to support the heat of its body than would have been necessary had it been protected from the cold. But in the evening it was removed into a warm and well-littered stall, where the warmth thus communicated was equivalent to a certain amount of food; and hence we find, that the milk of the morning was considerably richer in butter. It is uniformly found to be the case, that a stall-fed cow yields more butter in its milk than one fed in the field. Besides the warmth of the shed, less butter is consumed by the oxygen of the air. In the stall the respirations of an animal are much less frequent than in the field, and consequently less oxygen enters into its system. The great care of all dairy farmers is to prevent an excess of this gas from entering the body. Hence the practice of milking in the field those cows which are distant from home, and of driving home to be milked only such cows as are close to the shed. The exercise required in walking home causes an increased play of the respiratory system, and therefore increases the amount of oxygen inspired. This oxygen unites with part of the butter and consumes it. The greatest care is taken by all good dairymen to allow the cows to walk home at their own pace, and never to accelerate it. By this means only a small amount of oxygen enters the system. When a cow is harassed and runs to escape from the annoyance, its milk becomes very much heated, diminishes in volume and in richness, and speedily becomes sour. This is a fact well known to all dairymen. During running the cow respires a large quantity of oxygen. This unites with the butter, and the

heat evolved by its combustion elevates the temperature of the milk and evaporates part of its water. The acetous fermentation is also induced, and cannot be restrained. For this reason cows are not turned into the fields in very hot weather, when the flies are apt to annoy them and produce restiveness. During such weather, it is not an uncommon practice to feed the cows in the stall during the day and turn them out to grass at night. By this means they are kept tranquil, and prevented from respiring a large amount of oxygen. There cannot be any doubt that the practice of stall-feeding cows during winter or in cold weather must conduce very much to the formation of butter; but in summer, when the pastures are rich and near the dairy, the slight exercise which they receive increases their health, and with it their appetite. They are thus induced to eat more food than they would do in the stall, and they consequently receive a greater flow of milk. The loss experienced by the greater absorption of oxygen is more than compensated for by the increased appetite of the animal.

In these experiments it will be remarked, that potatoes were favourable both to the flow of milk and formation of butter. This quite accords with practical experience. They abound in starch, and therefore furnish the substance from which butter is formed. The increase of butter in the milk of the fourth day is very striking; on this day 24 lbs. of potatoes formed part of the food. The butter is also in large quantity in the milk of the fifth day, though not so much so as in that of the fourth, though 6 lbs. of potatoes in excess were consumed. In these 6 lbs. of potatoes only $1\frac{1}{2}$ lb. of dry unazotised matter were furnished, which could not compensate for 8 lbs. of beans (containing 4 lbs. of dry unazotised matter) which had formed part of the diet of the preceding day. The result is, therefore, exactly as might have been anticipated. When the food contained much starch, the sugar of milk increased in quantity as well as the butter. The large amount of butter in the milk of the second day is singular, and makes us regret the accident which happened to the milk of the morning and prevented its analysis. A remark has often been made to me by practical men (how far it is true I know not), that the milk of the morning is generally richer than that of the evening. As far as the limited number of analyses here given warrants any conclusion, there would seem to be some accuracy in this observation. The cause that it should be so is apparent: during the day, when exercise is taken, the number of respirations is frequent, and a large amount of oxygen enters the system—this is unfavourable to the formation of butter; but at night, during sleep, the respirations

are slow, and the amount of oxygen respired is trifling. Such a condition must favour the separation of oxygen from starch to supply the deficiency.

All practical experience is against the theory of Dumas, regarding the formation of butter in milk, and of fat in cattle. In Scotland the system of stall-feeding cows is carried to a great extent. The Glasgow dairymen feed their cows in warm stalls, giving them malt refuse, a few pounds of beans, steamed turneps and potatoes, and as much pot ale (residuum after distillation, commonly called wash) as they will drink. The malt refuse consists of starch, gum, and a little saccharine matter, but it is not known to contain fat. This refuse is the principal food, and is very favourable to the production of butter, evidently from its great excess of unazotised matter. The beans furnish the nitrogenous matter, in which the other foods are deficient; and as they contain casein ready formed, they assist in the formation of the milk. Their value is fully appreciated by all Scotch dairymen, although their use is little known in this country. The pot ale contains sugar and alcohol, and therefore contributes to sustain the heat of the body. It thus enables the other food to be formed into butter. But its principal use seems to be in diluting the secretions. Pure water does not readily enter the blood; we know that it destroys the blood-globules. But acid water does not do so, and this pot ale is generally very acid. Hence it dilutes the secretions. The great object, therefore, in this kind of feeding, is to give the cows as much unazotised food as possible; and the food which is preferred, consists of those very kinds in which fat exists in the least proportion. Porter and beer are well known to be favourable to the production of butter in the milk both of women and of cows; yet these fluids do not contain fat. We are, therefore, justified in asserting that practice is opposed to the theory of Dumas, but highly favourable to that propounded by Liebig.

During stall-feeding we have it in our power to alter the composition of milk, even with respect to the casein. Thus in the second day the cow received in its food $2\frac{1}{2}$ lbs. of albumen, or of a substance of the same composition (28 lbs. of hay, $2\frac{1}{2}$ lbs. of oatmeal). It produced 19 lbs. of milk, in which was 0·93 lb. of cheese. The next day it received 5 lbs., or double the quantity, of albumen in its food, and the milk, which amounted to 22 lbs., contained 1 lb. of casein*. Still theory would have led us to anticipate a larger increase than actually took place. The circumstance which favoured the production of casein in the milk of the first day will afterwards be considered.

* Calculated according to the composition of the evening's milk, as that of the morning had not been analysed.

The cow received in the food given on the fourth day, 4 lbs. of casein and albumen (14 lbs. hay, 8 lbs. beans, 24 lbs. potatoes), and yielded 23·22 lbs. of milk, which contained 0·75 lb. of casein. The fifth day she received considerably less albumen in her food, viz. 1·7 lb. (14 lbs. hay and 30 lbs. potatoes), but the amount of casein in the milk, though in less per centage than before, was equal in amount to the other, from there being a greater flow of milk. The milk amounted to 25 lbs., of which about 0·94 lb. was casein. Here, although the food did not contain much casein, it was such as to induce a great flow of milk, and the casein must have been derived from the albumen of the blood. Had the cow been continued on this food, there cannot be a doubt that the quantity of casein in the milk must either have diminished, or the cow must have lost condition in giving this substance at the expense of its tissues.

The value of these experiments is certainly very much diminished by not being extended over a series of days on each kind of food. But in England, where the price of æther is so exorbitantly high, the expense of such experiments is a serious consideration for a private individual. As they were conducted under the same conditions with respect to temperature and exercise, an indication of the effects produced by the various foods must have been obtained, although the final effects have escaped detection.

Neglecting the second day, in which an abnormal increase of casein was produced by an accidental circumstance, we find the milk of the third day contained 5·4 per cent. of casein, that of the fourth 3·9 per cent., and of the fifth also 3·9 per cent. The food consumed on the third day contained a very large amount of casein, and this was immediately followed by an increased amount in the milk. Some peculiar cause favoured the flow of milk on the fifth day, in spite of the small quantity of albumen in the food; the milk derived its casein from other sources. The milk of the second day contained 4·9 per cent. of casein, while that of the fourth day possessed only 3·9 per cent. of the same constituent, although on that day the cow had received 4 lbs. of albumen in its food, and on the former day only one half or 2 lbs.

Such are the changes which constantly occur to the dairy farmer, and cause variations in the value of his milk, even when the conditions of feeding seem to be the same. It is for us to determine to what these seemingly discordant results are due.

In experiments such as these, we must remember that the animal body is not a mere chemical laboratory, in which a chemist may operate as he pleases. But there is a power,—

vitality,—superior to his, and it is only by its concurrence that the changes which he desires are effected.

Now, on the second day the animal struggled violently to regain its liberty, and consequently expended much matter in the production of force. It is difficult to conceive that any waste of tissues can take place, without an alteration in their chemical composition. Still we cannot deny (in the present state of our knowledge) that an alteration in form might effect a waste, as well as a change in composition. We know little or nothing of the nature of secretion. All we know is, that certain glands have the power of appropriating particular parts of the organism or of food, and of producing fluids, which either perform some new functions in the system, or are separated from it; but we are entirely ignorant how these secretions are produced. Scherer has indeed pointed out that albumen may be converted into casein by digestion with caustic potash; and it is possible that this may be the process employed to form it in the organism. On this view, we might suppose that the waste of the tissues operated indirectly in its production. By their waste their alkaline constituents are liberated, and might act upon the albumen of the blood by converting it into casein. Be this as it may, there are many facts which induce us to believe that the waste of the tissues does favour the production of casein in the milk. The milk of a cow, fed in the stall, is not only absolutely but relatively poorer in casein than one fed in the field, where exercise increases the transformation of its tissues. During parturition all the muscles are thrown into a violent state of action. As the labour in a cow continues for many hours, there must be a great waste of tissues in the production of the force necessary to occasion these muscular exertions. Such being the case, if our view be correct there ought to be in the milk of a cow, immediately after parturition, an abundance of casein: and every one knows that such milk is quite thick with cheese. We are indebted to Boussingault for an analysis of the milk of a cow before the calf had been allowed to suck. He found it to contain as much as 15 per cent. of casein, while the milk of the same cow analysed a few days after its calving contained only 3 per cent. of the same substance; therefore only one-fifth the quantity*. If then the waste of the tissues tends, directly or indirectly, to increase the amount of casein

* It might be objected to the view given, that the analysis of this milk indicates a very small amount of inorganic ingredients. Boussingault found only 0·3 per cent. To this it may be answered, that the alkalies which favoured the formation of casein are soluble, and therefore were neglected in Boussingault's analysis, by being included along with the sugar of milk. (*Ann. de Ch. et de Phys.* lxxi. p. 72.)

in the milk, then we are at no loss to understand why the milk of the second day should be unusually rich in casein.

Beans contain 31 per cent. of casein ready formed. Hence it is that they have been found so practically useful in aiding the formation of the milk.

The conditions necessary for the production of casein in the milk, are different from those which are favourable to the formation of butter. When butter is the principal object desired, the cow cannot be put upon too rich pastures. But in all cheese districts, it is agreed that *poor* land is best adapted for cheese. Land is called poor, not when the grass is deficient in nitrogenous bodies, but in constituents destitute of nitrogen. The "equivalent," as farmers term it, is higher; that is, the cattle are compelled to eat a greater quantity of poor than of rich grass, in order to sustain animal heat. They have also to traverse more ground to procure their food; this causes an increased respiration of oxygen and waste of the tissues. Hence the appetite of the animal is increased, and a larger quantity of food is consumed. If the view already given be correct, the waste of the tissues aids in the supply of casein to the milk. One great object in cheese-farms is to induce the cows to eat a large quantity of food, and for this purpose, in large farms, they are tempted with new pastures every day. The Cheddar, Cheshire and Stilton cheeses contain a considerable quantity of butter. In a celebrated cheese-farm, a few miles from Bridgewater, where Cheddar cheese is made in great perfection, I found it to be the practice (a prevalent one, I believe) to drive the cows in the morning to the pastures on dry sandy soil, and in the evening to those situated on soft peaty soil. The grass of the sandy soil being poor, the cows traversed considerable ground in procuring it. They therefore eat a quantity more than they would have done on rich land, where there is little exertion required in taking the food. By this means a large quantity of cheese was procured in the milk. But during the night they were allowed to feed on rich pastures, fitted for the formation of butter, and as the darkness prevented them from wandering, little oxygen was respired to consume the butter formed, or to prevent its formation. The milk of the evening and morning being always mixed together in the preparation of the cheese, a proper proportion of both constituents was thus procured. In districts where inferior cheeses are manufactured, that is, in which the farmer depends upon his butter as much as upon his cheese, he is ignorant of the value of poor land. Thus it is that there is occasionally a contradiction amongst dairymen with respect to this point, though there is

none with those who depend wholly on their cheese, and care little for the butter, except as a means of enriching the former.

Chevallier's analysis of woman's milk (the only one of which I am aware) indicates a very small quantity of butter. As attention to diet and exercise must be very important to nurses, when we consider the trivial causes which produce a variation in the composition of milk, I was desirous of ascertaining whether the quantity of butter could be made greater than in the analysis given by Chevallier. Accordingly I selected a farmer's wife, a strong healthy female of twenty-eight years of age, who had been delivered of her third child. On the 19th day after her confinement she remained in bed, and thus diminished the amount of oxygen respired, and was then fed upon gruel (oatmeal and water). On the 21st sufficient milk for analysis was procured.

23·945 grammes yielded—

Casein	0·3695	1·54
Butter	1·0315	4·30
Sugar of milk. .	1·3770	5·75
Ashes	0·1270	0·53
Water	21·0400	87·88
	23·9450	100·00

The butter in this milk was therefore quite equal to that in the milk of a cow. As the diet thus influences the composition of the milk, may not the frequent occurrence of ricketty children in the higher classes of life be due to the circumstance of the mothers living principally upon white bread—bread, therefore, from which phosphates have been in a great measure removed? Had the woman been at her usual exercise, it must of course have diminished. The milk of a woman possesses a very sweet taste, and is remarkable for its great amount of sugar of milk. In this and in other respects it closely resembles that of the ass. The following analyses exhibit the composition of the milk of various animals :—

	Woman.		Ass.		Cow.		
	Henry and Chevallier*.	Playfair†.	Peligot‡.	Henry and Chevallier.*	Bousingault†.	Henry and Chevallier*.	Playfair‖.
Casein . . .	1·52	1·54	1·95	1·82	3·2	4·48	4·0
Butter . . .	3·55	4·30	1·29	0·11	4·1	3·13	4·6
Sugar of milk	6·50	5·75	6·29	6·08	5·1	4·77	3·8
Ashes . . .	0·45	0·53	..	0·34	0·2	0·60	0·6
Water . . .	87·98	87·88	90·47	91·65	87·4	87·02	87·0

* *Journal de Pharmacie*, xxv. 333 et 401. † *Suprà.*
‡ *Ann. de Ch. et de Phys.* lxii. 432.
§ *Ann. de Ch. et de Phys.* lxxi. 65.
‖ Average of analyses of the milk of a cow in the field.

Before concluding this paper, I take the opportunity of making a few remarks to *practical men* on the mode of preserving milk, as this is a subject on which questions have been often sent to me.

Milk consists of casein, of sugar of milk, and of certain salts dissolved in water, in which are suspended little globules of fat or butter. These globules are surrounded by a shell or skin, which is supposed (by Otto) to be coagulated casein. The soluble casein, being a nitrogenous body, is very apt to run into putrefaction. In summer it does not do so readily, because the temperature being elevated, the sugar of milk is converted apparently into grape sugar by the agency of lactic acid, then into alcohol, and the alcohol into acetic acid. These changes are induced by a primary action of oxygen upon the casein. This action is then imparted to the other constituents, the atoms of which being once set in motion, readily undergo the changes described. The acetic acid being formed by the agency of air on the alcohol, acts upon the soluble casein and coagulates it, or renders it insoluble. It is thus removed from the action of the oxygen of the air, and may be kept for some time without entering into putrefaction. Such are the changes which milk undergoes in summer, but they are quite different in winter.

In winter the first action is that of oxygen upon the casein. The temperature is not sufficiently elevated to cause vinous fermentation. The decay of the casein generally passes over to putrefaction, that is, the atoms are transformed more rapidly than they unite with oxygen. A putrid smell now arises.

Good butter cannot be made from milk which has undergone this change. The cause is, that butter always contains a certain quantity of casein which it is difficult to remove. When incipient putrefaction has taken place, it cannot be arrested by ordinary means, and imparts itself to the bodies with which it is in contact. It is for this reason that the greatest part of the butter manufactured in winter has a rank putrid taste.

The principal object in view in the preservation of milk in winter, is to prevent the commencement of this putrefaction. One method has been termed *scalding* the milk, and is generally used in dairies. It consists in heating the milk until the oxygen of the air acts upon the casein, and forms a pellicle on its surface. The milk should then be left to perfect repose. The pellicle excludes the air from the soluble casein. The partial oxidation by which the pellicle was produced, is effected at too high a temperature to enable the decay to pass into putrefaction. When this operation is skilfully performed,

the milk remains quite good for four or five days. But there is a risk of failure in this process, and it is only adapted for small dairies.

The best method, which I have seen used in practice with much success, seems to be to induce the acetous fermentation in the milk. For this purpose, the cream or milk, being placed in a proper vessel, should be surrounded with hot water. The heat which I find to answer best is from 100° to 110°. A cloth may be thrown over the whole to retain the heat, and as the water cools, it should be removed and replenished with hot water of the above temperature. In a few hours the cream acquires the smell and taste of vinegar. The changes which I have described above ensue. In large dairies a portion of this soured cream or milk may be added to fresh cream or milk, which should be kept in a room possessing a temperature of 60°. By adding this soured cream to the fresh milk, we furnish an acid, by which the sugar of milk is converted into grape sugar. The curd then acts upon the grape sugar, and converts it into alcohol. The latter by oxidation becomes acetic acid, and thus the whole mass of milk is rendered sour, the casein coagulated, and therefore protected from immediate putrefaction. The butter made from such soured milk is quite sweet and destitute of that rank taste which distinguishes our winter from summer butter. But if incipient putrefaction has once begun in the milk, all this will be of no avail, because it is communicated to the insoluble casein. Milk perfectly fresh must therefore be used. Fresh milk soured in this way will last for many days, and give risings of cream for a considerable time. This practice, as far as I am aware, is not a general one, though it is well worthy of adoption. In summer of course no such operation is requisite, as it is done at a sacrifice of the skimmed milk. One great cause of the putrefaction in milk is the want of absolute cleanliness in the dairy. If a drop of milk fall on the table, it should be dried and washed off with care, for its putrefaction causes the evolution of a putrid gas, and this *imparts* its state of putrefaction to the remainder of the milk.

With respect to making butter, scientific explanations can be of little use to practical men. The theory of churning is very simple. By agitation, the globules of butter are broken, and made to unite together into a mass. The introduction of air during churning, aided by the heat at which the cream or milk is, occasions the formation of lactic or acetic acid, and this coagulates the casein, and thus assists the separation of the butter. In summer, when the heat prevents the ready coherence of the butter, a quantity of cold spring water thrown

in, after the buttermilk has formed, often effects the desired end. The temperature is thus depressed, the butter rendered solid and more coherent, while the air contained in the water aids in the formation of acid and coagulation of the casein. The only thing, in a scientific point of view, to attend to after the separation of the butter, is to free it from buttermilk or casein. If the casein be suffered to remain, putrefaction ensues, and the butter acquires a rank putrid taste. Its separation is therefore of the first moment.

The cause of the superiority of certain foreign butter, which retains its flavour and taste for a considerable time, is more due to its freedom from casein than to any mystery in its mode of preparation.

XXXI. *On a new Method of obtaining pure Silver, either in the Metallic State or in the form of Oxide.* *By* William Gregory, *M.D., F.R.S.E., &c.*

Read February 7, 1843.

THE chemist, as well as the metallurgist, has frequent occasion to purify silver, especially from copper, which is dissolved along with it by nitric acid, the proper solvent of silver. By converting the silver into the insoluble chloride, it is effectually purified from copper as well as from all other metals, the chlorides of which are soluble. But here the difficulty begins: the chloride of silver is a very unmanageable product, at least in the moist way. It is true that if placed in water acidulated with hydrochloric acid, in contact with zinc or iron, the chloride of silver is reduced. But the process is tedious, seldom complete, and in the end unsatisfactory; for some zinc adheres to the reduced silver, so that it is not removed by digestion with moderately strong hydrochloric acid. This is proved by the action of ammonia, which extracts a good deal of oxide of zinc. Moreover, the zinc or iron is hardly ever pure; and its impurities, arsenic, carbon, and perhaps also copper and tin, remain with the silver. I have never got from silver thus reduced, a colourless solution of nitrate.

It is no doubt better to decompose the dried chloride of silver by the action of carbonate of potash or soda at a red heat. But although the silver is thus obtained pure, the process requires much experience and dexterity. If the heat be too low, the reduced silver is disseminated in small globules through the mass; if too high, the alkali corrodes the crucible rapidly, and the contents fall into the fireplace or ash-pit. There is often also a portion of silver cast up by the effer-

vescence on the sides of the crucible, in small globules, which do not readily run down into the fused mass below. In short, this process, always ticklish, often fails. It is therefore desirable, if possible, to dispense with a furnace heat.

The method of reducing the silver from the impure nitrate by protosulphate of iron does not answer. It is long ere the action is terminated, and besides, some sulphate is always formed, which *is not reduced*, and is partly precipitated with the metal, and partly retained in solution.

The only remaining method, known to me, is that of reducing the silver from the impure (cupreous) nitrate or sulphate, by means of copper. The chief objection to this method is that it is somewhat tedious; but it is also not improbable that a trace of copper may adhere to the silver, chemically combined, as is the case to a large extent with mercury in the *Arbor Dianæ*. At least I have generally found copper in the silver I have thus prepared.

Considering these things, it appeared desirable to have once more recourse to the chloride, which can be easily obtained perfectly pure, and to decompose it without the contact of any reguline metal. The most obvious plan was to try the action of caustic alkalies in the moist way, and although it has been singularly enough hitherto overlooked, I find that caustic potash may be used with complete success. Diluted potash, or even a concentrated solution, if cold, has no apparent action on chloride of silver; and this, I presume, explains how the reaction about to be described has not been noticed. But a solution of potash, spec. grav. 1·25 to 1·30, with the aid of heat, decomposes almost instantaneously the moist chloride of silver, converting it into a heavy, fine jet-black powder, which is pure oxide of silver. This oxide dissolves without the smallest residue, and without effervescence in diluted nitric acid, and yields a colourless and pure nitrate. The heat of the spirit-lamp reduces the oxide to a coherent spongy mass of absolutely pure silver.

The following method appears to me the most advantageous.

The cupreous solution of silver is precipitated by common salt, while hot, and the chloride of silver well washed by decantation with hot water. It should also be broken down with a spatula of platinum or a glass rod, during the washing, but not ground in a mortar, which causes it to cake, and impedes the action of the potash. The chloride, *while still moist*, is covered to about half an inch with a solution of caustic potash, spec. grav. 1·25 at least, and then boiled. During the boiling, which is best performed in a capsule of clean iron, silver, or platinum, the chloride is to be well stirred, in order to

bruise all curdy or lumpy particles. In five or ten minutes the powder has become black. If a small portion, taken out and washed, do not dissolve without residue in dilute nitric acid, the potash is to be decanted off, and the powder, still moist, is to be well rubbed down in a mortar, which may now be done with advantage. It is then returned into the capsule, and again boiled for five minutes with the same, or with fresh potash. It will now dissolve entirely in nitric acid; but if not, a second grinding will infallibly succeed. It is now only necessary to wash the oxide, which is completed by decantation in a few minutes, as the powder, from its great density, sinks at once to the bottom. The first two or three washings are made with hot water, the remainder with cold water; for when the oxide is nearly washed, it rises partially to the surface, *with hot water*, and thus a loss is occasioned in decanting. Of course, the whole washings (except the first, owing to the strength of the potash) may be conducted on a filter. But the powder is so fine, that probably a good deal would adhere to the paper when dry.

This oxide of silver appears in a form quite distinct from that of the oxide precipitated by potash from the nitrates, and is hitherto undescribed. It is very dense, homogeneous, and has a pure black colour, which has, if anything, a tint of blue; whereas the common oxide is bulky, far less dense, and of a grayish brown colour. They appear, however, to be chemically identical. Not having a microscope, I have not studied their physical characters minutely; but I suspect, from its aspect in the liquid in which it is formed, that the new oxide is crystalline.

It is obvious that the above process furnishes an easy method of procuring a very pure oxide of silver, and of course the action of heat gives us the silver in the state of metal. It is, I conceive, applicable both to the manufacture of nitrate (in a state of absolute purity) and to the metallurgic process for obtaining pure silver. For both objects, it is a matter of no consequence, if some chloride should have escaped the action of the alkali. This chloride is left undissolved by the nitric acid, and is separated by filtration; while if the oxide (not quite free from chloride) be mixed with a little nitre or carbonate of potash, and fused, the whole silver is obtained with the utmost facility*. In order to give an idea of the ease with which the whole is performed, I may mention that

* In fact, this process, imperfectly performed, is an excellent preliminary step, when a large quantity of chloride is to be reduced. The impure oxide requires so little alkali to complete its decomposition, that the crucible runs no risk. A little borax may be added as a flux.

I dissolved a half-crown, and obtained the whole of the silver it contained, within a very trifling fraction (chiefly decanted in the *first* washing of the chloride, *but not lost*), by the above process, *within two hours*, in a fused state. The silver was quite pure. There is no doubt that to chemists also an easy method of obtaining quickly pure oxide of silver, in a form much less hygrometric than the usual one, will be acceptable.

It is particularly to be noticed, that if the chloride have *once been dried*, it is with great difficulty decomposed, even by a long boiling with potash.

XXXII. *The Leaf-stalks of Garden Rhubarb as a Source of Malic Acid.* *By* Thomas Everitt, *Esq.*

Read February 7, 1843.

THE large quantity of this substance which is brought to our vegetable markets for several months in the year, beginning very early in spring, and its powerful though agreeable acid taste, make it a subject worthy of a more minute chemical examination than any which it has as yet been subjected to.

The leaf-stalks of garden rhubarb were first examined by Mr. Henderson*, who discovered in them, as he thought, a peculiar acid; afterwards by M. Lassaigne†, who showed that the supposed new acid was oxalic acid. But these experimenters examined only the precipitate obtained by putting chalk into the expressed juice; the first-named decomposing the insoluble precipitate thus obtained by sulphuric acid; the other, by boiling it with excess of carbonate of potassa, then neutralizing the solution with nitric acid, and precipitating by a salt of lead, decomposing the latter by sulphuretted hydrogen, and thus getting crystals which were oxalic acid. Now by both these processes, those chemists threw away, in the liquid which floated above the oxalate of lime, an important constituent in a large quantity, viz. malate of lime, with a great many other things of less importance, but which rendered the devising of a process for obtaining the principal ingredients pure, a difficult analytical problem. The details of the preliminary experiments (which occupied some time) for finding out what I had to deal with, would be both tedious and useless; I proceed, therefore, to give a summary of the method I adopted for the analysis of this substance, and of the best

* 'Thomson's Annals of Philosophy,' vol. viii. p. 247. (1816.)

† *Annales de Chimie et de Physique*, tom. viii. p. 402. (1818.)

means of proceeding, if the extraction of malic acid be the only object. The stalks should have the cuticle taken off, as it would introduce a great deal of colouring matter if put into the press; the peeled stalks are cut into small pieces about an inch long, put into a strong canvas bag, and then subjected to a great pressure; by this means 20,000 grains of peeled stalks, yielded 12,500 grains of juice, and left 3850 grains of damp fibre, which well washed and dried at 212°, weighed 800 grains, and is equal to 4 per cent. ligneous fibre. The liquid had a light green colour, was very acid, its density varied with the size of the stalks and the time elapsed since they were cut, it also varied in the same specimen at different periods of the pressing; that which flows first I have had as low as 1·015, rising to that last yielded 1·022.

I tried how much pure carbonate of soda and carbonate of potassa were required to saturate a definite quantity; but as it afterwards was found to contain two or three acids, and some salts of soda and potassa also present, these results are of no use for determining the quantity of free acid. Some pure crystals of carbonate of lime were made into a neutral nitrate; chloride of calcium being avoided as in a subsequent stage chloride of lead, and hydrochloric acid would be formed, to get rid of which would have complicated the process.

To several pints of the juice bicarbonate of potassa was added, this salt being used because it is much purer than the carbonate, until all acidity was neutralized: a small quantity of greenish pulpy matter made its appearance, which was separated by a cloth filter, and the liquid became much less coloured: 4000 grains measure, specific gravity 1·012, required 65 grains of crystallized bicarbonate potassa for neutralization: 4000 at 1·023 required 93 of the same for neutralization: nitrate of lime was now added and the solution boiled: this is necessary, because oxalate of lime, when precipitated cold and thrown on a paper filter without boiling, passes through; moreover, malate of lime requires only 65 parts of boiling water to hold it in solution. I found the separation of the oxalic acid perfect by these means, while all the malates remained in solution. The oxalate of lime collected on the filter, amounted to 24·2 grains, dried at 212°, or the protohydrate. It was tested in the usual way of boiling with excess of carbonate of soda or potassa, filtered, neutralized with nitric acid, and precipitated by nitrate of silver; the powder dried and heated exploded feebly in the manner peculiar to the oxalate of silver, leaving metallic silver. Nitrate of lead was now added to the solution which had passed through the filter from the oxalate of lime, and a copious bulky precipitate

was formed, which the next day, when it was cold, had formed on its surface a few of the beautiful flat pearly crystals characteristic of malate of lead: it was brought to the boil, and the malate of lead assumed a consistency like dough before it goes into the oven; and when that cooled it became as brittle as resin. The liquid above the solid mass was decanted and yielded good crystals on cooling. The whole malate of lead was carefully washed and elutriated. About two-thirds of it was acted on afterwards by sulphuric acid gently heated; then separating the sulphate of lead by a filter, the remaining third of malate lead was suspended in the liquid, and sulphuretted hydrogen passed through it till all the malic acid was set free. This decomposition of some of it by sulphuretted hydrogen, renders the solution sufficiently colourless, while to do the whole in this way is very tedious. When operating on several ounces, after filtration to collect the sulphuret of lead, the free malic acid must be evaporated by a water or steam bath to the thickness of syrup; and it was only obtained of the consistency of thick honey, by keeping it under the receiver of an air-pump, near the surface of oil of vitriol, for nearly a week, occasionally taking out the capsule to warm it. Some of the original juice evaporated in the same way, yielded beautiful crystals of binoxalate of potassa.

After this the liquor still retained a small trace of citric acid, which I obtained in a distinct form by taking advantage of the difference of the solubility of malate and citrate of baryta. No tartaric could be detected.

4000 grains of the original liquid evaporated and ignited in platinum, yielded 29·2 grains of ashes, of which

28·4 grains were soluble in water, and 0·8 insoluble.

The solution of these 28·4 grains was alkaline, and required 12 real nitric, or 8·9 of sulphuric acid to neutralize it (these two acids were used of an exact strength so as to contain 1 grain of real acid in 100 grains water measure). To the neutral solution of the ashes in sulphuric acid nitrate of baryta was added; a precipitate was formed, part of which was soluble on adding a little nitric acid, and turned out to be phosphate. The insoluble sulphate weighed 39·73 grains: no lime salt was present. The nitric acid solution of the phosphate evaporated to dryness left 4·4 grains; it was well tested and certainly proved to be phosphate, being made into an alkaline phosphate and tested by silver and other means. To the solution which filtered from the mixed sulphate and phosphate, containing excess of nitric acid, nitrate silver was added and 4·1 of chloride obtained; to the solution filtered from the chloride of silver, excess of hydrochloric and sulphuric

acids were added to remove the excess of silver and baryta: the filtered liquid evaporated to dryness and ignited, after putting on it excess of sulphuric acid, gave 39·3 grains of a white salt, quite soluble in water (sulphates of soda and potassa); these were dissolved in a minimum of water, and excess of crystals of tartaric were added; the granular precipitate washed with dilute alcohol, weighed 33·3; the solution from the bitartrate of potassa evaporated and ignited, then treated with sulphuric acid, evaporated again to dryness and ignited, gave of dry sulphate of soda 4·7; this was dissolved in water, and being slowly evaporated, the characteristic crystals were formed.

From the above data, and from some subsequent experiments on a much larger quantity of juice, an imperial gallon (sp. gravity 1·022), contains nearly, of

Malic acid dry	11139·2	grains.
Oxalic acid dry	320·6	„
Potassa combined with organic-chloride, soda, sulphuric and phosphoric acids, traces of silicon and a little vegetable extract	229·6	„

If to obtain malic acid be the only object, slaked lime made into a sort of cream with water might be added to the expressed juice, till the solution became slightly alkaline; it might then all be boiled and filtered, then proceed with the nitrate of lead and the rest of the steps above described. To procure the malate of lead in good crystals, some precautions are necessary. From the precipitate suspended in water and heated, a few grains only fall on cooling; from 2 pints I only obtained $5\frac{1}{2}$ grains; but if about 2 per cent. of acetic, or of some free malic, be added to the water, and finely divided malate of lead be added, and the whole warmed by a water bath, with constant stirring, the quantity of crystals will be doubled for the same bulk of liquid. It is proper not to raise the temperature higher than 160° Fahr.; if boiled the salt loses two or three atoms of its water of crystallization, and then is quite insoluble in water hot or cold. The composition of malic acid is exactly the same as that of citric acid, $C_4 H_2 O_4$.

The crystals of malate of lead are thus constituted:—

1 proportion of acid . . .	58	...	29·68
1 proportion of oxide of lead	112	...	56·62
3 proportions of water . .	27	...	13·70
			100·00

100 grains of the crystals exposed in a thin stratum on a

porcelain dish, can lose at 212° 9·2 water = 2 proportions, but it required to be heated in a thin glass tube, by means of an oil-bath to 356° Fahr. before it lost the other third. When the crystals are boiled in water, they lose also 2 proportions of water, and assume the form of dough after it has been kneaded; the mass on cooling becomes as brittle as resin.

XXXIII. *Observations on* M. Reiset's *Remarks on the New Method for the Estimation of Nitrogen in Organic Compounds, and also on the supposed part which the Nitrogen of the Atmosphere plays in the formation of Ammonia.* *By* H. Will, *Ph. D.*

Read March 21, 1843.

THE method for the estimation of the nitrogen in organic substances described by Varrentrapp and myself* has been received by many chemists with the greatest approbation, as well on account of its simplicity as the accuracy and security with which results can be obtained. M. Reiset has however presented an essay to the Academy of Sciences at Paris†, in which he endeavours to prove by experiments, at first sight very convincing, that the above-mentioned method is attended by two sources of error; the first of which in particular, were it true, would be quite sufficient to destroy completely the value of the method.

The cause of this first and principal source of error is, according to M. Reiset, that the nitrogen of the atmosphere forms a portion of the ammonia produced by the decomposition of nitrogenous matter by means of an alkaline hydrate, and that consequently too large an amount of nitrogen must always be obtained, particularly in bodies rich in carbon, bodies of difficult combustion, and those which readily form cyanogen compounds. This source of error becomes the more important, as from the experiments of Faraday‡, which are confirmed by Reiset, it appears that by the fusion of many non-nitrogenous bodies with the hydrates of the alkalies a pretty considerable quantity of ammonia is formed. To those non-nitrogenous bodies which produce ammonia sugar in particular belongs, a substance which we proposed as an addition to other bodies for the purpose of diminishing the violence of the absorption of the ammonia by the hydrochloric acid.

The numerous analyses of nitrogenous bodies made by

* *Annal. der Chemie*, b. xxxix. s. 257.

† *Compt. Rend.*, vol. xv. p. 154; and *Annal. de Chim. et de Physique*, 3rd Ser. vol. v. p. 469.

‡ Quarterly Journal of Science, vol. xix. p. 16; and Poggendorff's *Annalen*, vol. iii. p. 455.

Varrentrapp and myself, must therefore have given a very considerable excess of nitrogen, if any formation of ammonia from the sugar really took place, and would be a constant source of error: it would be particularly evident in the analyses of ammeline, in which we mixed the substance with an equal weight of sugar. The accuracy and strictness of the results obtained by us from substances of well-known composition could therefore be ascribed only to accident, or perhaps to some source of error balancing the one just mentioned.

We thought we had met every objection of a source of error on this point by the experiments mentioned in our paper, in which we passed nitrogen and hydrogen gases through a glass tube over a red-hot mixture of carbonized bitartrate of potash and lime, or of pure charcoal soda and lime, and from which we did not obtain sufficient ammonia to be estimated as ammonio-chloride of platinum; and yet all the conditions necessary for the formation of ammonia and cyanogen were afforded in the mixture of soda, lime and carbon by the hydrogen becoming free from the combustion of the carbon at the expense of the oxygen of the hydrated water, as well as through the difficulty of its combustion.

M. Reiset appears to have overlooked the fact that finely divided carbon is, as well as an organic substance, oxidized completely by means of the hydrates of the alkalies, and states that we have neglected to prove in a satisfactory manner, that the facts observed by Faraday (according to which non-nitrogenous bodies, as sugar, acetate of potash, oxalate of lime, tartrate of lead, &c., by ignition with potash, soda, or hydrate of barytes and access of air, give an appreciable quantity of ammonia), are without influence on the new process of analysis. He has undertaken this for us; and his experiments, which were made with stearine and sugar, gave him on combustion with soda-lime, under the same circumstances as in the execution of a nitrogen analysis, the following very remarkable results:—

Sugar.	Platinum obtained.	Nitrogen obtained.	Nitrogen in 100 parts.
0·250	0·02650	0·0038	1·52
0·500	0·05250	0·0075	1·50
1·000	0·0890	0·0127	1·27
1·500	0·104	0·0149	1·00
2·000	0·10725	0·0153	0·75

In these experiments the quantity of ammonia obtained was, as far as *one* gramme, in exact proportion to the quantity of sugar employed; with *more* sugar a greater quantity of ammonia was not obtained.

Reiset obtained further from one gramme of stearine, 0·06475 grm. of platinum = 0·0092 grm. of nitrogen, and in two other experiments with sugar performed in an atmosphere of hydrogen (from 1 gramme), 0·03375 grm. and 0·034 grm. of platinum = 0·0048 grm. of nitrogen.

From both these last experiments, according to which non-nitrogenous bodies also eliminate ammonia in an atmosphere of hydrogen, M. Reiset concludes that the alkaline mixture possesses the property of condensing nitrogen so intimately and strongly that it cannot be expelled completely by a current of hydrogen gas passed over it for six hours, and that this state of condensation, approaching as it does the nascent state, makes the nitrogen more apt to enter into combination.

As a further proof of the incorrectness of our method, M. Reiset brings forward the analysis of cinchovatina, an organic base discovered by Manzini in Jaën Cinchona, from an analysis of which, performed with a mixture of sugar, almost 5 per cent. more of nitrogen was obtained than the calculation required. Thus 0·052 grm. of cinchovatina gave 0·949 grm. of ammonio-chloride of platinum = 11·95 per cent. nitrogen. The calculation from the formula $C_{46} H_{27} N_2 O_8$ gives only 7·16 per cent.

The excess of 4·8 per cent. here obtained, estimated by weight, amounted to 0·024 gramme of nitrogen, or in volume nearly 25 cubic centimetres; in the above experiments with sugar 0·015 gramme of nitrogen was, according to M. Reiset, condensed in the soda-lime, and therefore took a part in the formation of the ammonia.

If we consider that the decomposition of organic bodies, of difficult combustion, by the hydrates of the alkalies does not take place at a heat below redness, that further, the heating of the contents of the tube by the fire placed around it cannot be so sudden as to produce in an instant the temperature necessary for combustion, but that the heat, even when sudden, penetrates the mixture only by degrees, and that the greater portion of the inclosed or condensed air is driven out by its own expansion, we can scarcely comprehend how M. Reiset could entertain the idea that the nitrogen condensed in the mixture could take a part in the formation of ammonia. He certainly brings forward an experiment apparently supporting this view, viz. that by the combustion of 1·500 gramme of sugar in a current of air, the combustion being thus quickened, only 0·0099 grm. of nitrogen was obtained, instead of 0·0149. This ammonia however did not increase when pure nitrogen was passed over the mixture during the combustion. I shall subsequently return to this point.

I have repeated and partly varied the experiments of Reiset, and have come to entirely different results.

1·214 grammes of sugar-candy of the shops by combustion with the usual mixture of soda-lime, which had not been previously ignited, gave on evaporation with chloride of platinum and ignition of the washed residue, 0·006 grm. of metallic platinum = 0·00086 grm. of nitrogen = 0·07 per cent. of the sugar burned.

0·386 grm. of pure stearic acid recrystallized from alcohol, gave 0·002 grm. of metallic platinum = 0·00028 grm. of nitrogen.

0·430 grm. of leguminous starch, prepared in the laboratory of Giessen, and purified with sulphuric acid, gave 0·005 grm. of metallic platinum equivalent to 0·0007 grm. of nitrogen.

A gramme of the above-mentioned starch was submitted to dry distillation. The product of distillation was mixed with hydrochloric acid, evaporated to dryness, the residue dissolved in water, mixed with chloride of platinum, and again evaporated to dryness. After treatment with alcohol and æther, a a portion of ammonio-chloride of platinum remained, which ignited left 0·004 grm. of metallic platinum. The ammonia obtained by the combustion with soda-lime was thus, in part at least, contained in the starch, and was no product of the operation.

In both the following experiments, conducted exactly as an ordinary combustion, I employed soda-lime ignited just before its introduction into the tube.

1·000 gramme of stearic acid decomposed with soda-lime in a tube 1½ foot long and half an inch wide, left, after evaporation to dryness with chloride of platinum and resolution in æther-alcohol, no visible trace of ammonio-chloride of platinum.

2·000 grammes of pulverized metallic tin, after ignition with soda-lime and treatment of the residue, after the evaporation of the hydrochloric acid, with chloride of platinum, afforded an extremely small quantity of yellow powder, which possessed all the properties of ammonio-chloride of platinum.

In the following experiments, a stream either of atmospheric air or of nitrogen gas was passed through the tube during the successive oxidation of the substance by means of an alkaline hydrate. Both the atmospheric air and the nitrogen were dried by means of sulphuric acid, which had been freed from nitric oxide by treatment with sulphate of iron.

The volume of gas passed through was about from three to four thousand cubic centimetres, and the combustion throughout the whole length of the tube was so conducted, the experiment lasting from two to three hours, that the conditions

necessary for the formation of ammonia were given at every moment.

4·000 grms. of perfectly pure recrystallized sugar, ignited in a tube 2½ feet long, with a large mass of soda-lime in a current of air, gave no trace of ammonio-chloride of platinum.

20 grms. of common pulverized tin, oxidized in the same way with soda-lime, gave a quantity of yellow powder, too small to be weighed. The uninterrupted disengagement of hydrogen proved, however, that the tin was oxidized at the expense of the alkaline hydrate.

4·300 grms. of recrystallized sugar were introduced by degrees through the tubulure of a retort whose neck was obliquely turned up, and in which soda-lime was in a state of fusion. An aspirator was attached to the absorption apparatus connected with the retort, so that the gaseous product formed, following the current of air, should pass through the hydrochloric acid. Only an extremely small trace of ammonio-chloride of platinum was obtained. The same experiment repeated with tin, zinc, and pure metallic iron, always afforded ammonio-chloride of platinum, yet so slight a trace that in most cases it did not admit of being estimated.

When hydrate of potash was employed instead of hydrate of soda, I always obtained potassio-chloride of platinum, because, from the violent evolution of the hydrogen, portions of the alkali were driven over into the hydrochloric acid. In another experiment 20 grms. of metallic tin were melted with fresh-fused hydrate of soda in a thin U-formed tube, with access of atmospheric air, so that during the continuance of the experiment a fresh quantity of air was always brought into contact with the nascent hydrogen; I obtained thus 0·008 grm. of ammonio-chloride of platinum = 0·00057 grm. of nitrogen. In an experiment in which nitrogen was used instead of atmospheric air, a similar result was obtained, namely 0·007 grm. of ammonio-chloride of platinum.

These experiments prove that the nitrogen of the atmosphere can in no way form ammonia with hydrogen in a nascent state. The extremely small quantities of ammonia obtained in most cases, and which it is very difficult to avoid, must consequently have some other source. This however may be attained by the following method:—

Hydrate of soda was melted in a silver crucible until it became liquid, and then mixed with a small quantity of pure iron, reduced from the oxide by means of hydrogen. This was readily oxidized with disengagement of hydrogen gas; it was then poured into a silver dish previously warmed, and after it had cooled was broken into pieces and introduced into a

slightly curved tube of hard glass half an inch in diameter, previously ignited; from 4 to 5 grammes of pure iron reduced from the oxide by hydrogen, were then immediately added; the tube was heated by charcoal placed under it, and nitrogen gas or atmospheric air passed through it. On the first passage of the air an extremely small quantity of ammonia was generally detected by means of dahlia-paper, or by a rod moistened with dilute hydrochloric acid; but this disengagement of ammonia was only observed for a short time, and always ceased before the evolution of the hydrogen, from the oxidation of the iron, began. When this took place it was connected with the absorption apparatus, and the alkali kept in a state of fusion until all the metal was oxidized. By carefully following this plan I never obtained ammonio-chloride of platinum.

The same experiment was repeated with a like result with perfectly pure crystallized tin, as it is easily obtained when a polished rod of tin is suspended in a vessel in which water with a little hydrochloric acid, rests on a concentrated solution of tin; after one or two days a splendid crystallization of the tin forms. If the metal happened to be touched by the fingers, or allowed to remain exposed to the air before the experiment, a disengagement of ammonia invariably occurred; but not when it as well as the alkaline hydrate were fused just before being employed. Pure tin is with great difficulty oxidized by hydrate of soda, and must be kept in a state of fusion with it for many hours before the oxidation is complete.

Reiset states that ammonia is disengaged by heating metallic iron and potash-ley to 292° Fahr., with access of air, but not so in an atmosphere of nitrogen. This statement rests on a very equivocal foundation. Pure iron can be heated for a long time in a boiling potash-ley without the disengagement of hydrogen; the oxidation takes place only on the fusion of the alkaline hydrates. If a quantity of potash-ley which has stood for a long time in a perfectly clean retort be heated, there is always observed at the commencement a slight disengagement of ammonia, but this soon ceases altogether.

The by no means inconsiderable quantities of ammonia obtained by Reiset, admit of no other explanation than that his mixture of soda and lime contained a nitrate, probably nitrate of potash, which, as Faraday states, easily evolves ammonia when the smallest trace of it is melted with zinc and an alkaline hydrate. If Reiset had only, in a small degree, followed or observed the extremely cautious and circumspect manner of proceeding of that celebrated English philosopher, a manner which is with justice admired by him, he would not

have endeavoured to find sources of error in a method to which, on this point at least, no very weighty objection can be made.

The nitrate of potash presumed to be contained in the soda-lime used by Reiset, was very probably owing to the circumstance that most manufacturers add a little of it to the commercial hydrates of soda and potash, for the purpose of improving their appearance. In Reiset's experiment, where he obtained 4·8 per cent. too much nitrogen in chincovatina, his mixture must have contained very nearly $\frac{1}{2}$ per cent. of nitrate of potash, when it is considered that his tube contained from 50 to 60 grammes. This also explains, in a much simpler and easier manner, the formation of ammonia in an atmosphere of hydrogen, and also the limited increase of ammonia from the increased quantities of sugar employed. As the whole quantity of nitrate of potash would be destroyed by from 1 to $1\frac{1}{2}$ gramme of sugar, the quantity of ammonia could not increase. The nitrogen was here certainly contained in such a condensed state, that a stream of hydrogen gas passed over it during twelve hours did not expel it.

I now come to the second source of error advanced, by M. Reiset, to the new method. It appears from his statements, that a part of the chloride of platinum is reduced to protochloride when the hydrochloric acid fluid, which in many cases contains liquid hydro-carburets, is evaporated to dryness with it in a water-bath; consequently too much nitrogen must always be obtained, as this protochloride of platinum is insoluble in æther and alcohol. And this source of error has the more injurious effects on the result the more its necessary conditions are afforded, and these conditions are the blackening of the hydro-carburets by the hydrochloric acid. In a direct experiment with sugar made for this purpose, and in which the burning was managed in such a manner that the hydro-carburets being produced at a low temperature floated in abundance on the hydrochloric acid, on evaporation in a water-bath no reduction of the chloride of platinum could be observed. It must be allowed, that in such a trifling case of occurrence, the result would not be affected by it. Indeed, the formation of hydro-carburets, easily decomposable by hydrochloric acid, may be completely avoided by keeping the nearer end of the tube pretty strongly ignited, as the hydro-carburets are the more constant when produced at high temperatures.

The highly remarkable and accurate experiments of Faraday on the disengagement or formation of ammonia by the fusion of hydrate of potash with a metallic or a non-nitroge-

nous body (a result which I have also found in all my experiments but which was so trifling that it could not be attributed to any part played by the nitrogen of the atmosphere), as also the investigation of Professor Liebig on the ammonia contained in rain-water, gives a complete and simple solution of the question, from whence comes this disengagement of ammonia so often observed and so difficult to be avoided.

The experiments of Faraday go entirely to show that there is some unknown source of ammonia, and that the nitrogen of the atmosphere in his experiments played no actual part; they are so convincing and made without any preconceived opinion, that I cannot refrain from giving a short extract from them here. They prove, as it appears to me, directly the reverse to the conclusion which M. Reiset has drawn from them, and are of the greatest importance in the question, whether the nitrogen of the atmosphere plays a temporary part in the formation of ammonia by the decay of organic matter, or by the oxidation of metals with or without the disengagement of hydrogen? An affirmative or negative to this question has a very important influence on the theory of the nutrition of plants.

Faraday observed that an organic substance, the quantity of whose nitrogen he wished to estimate, yielded ammonia by fusion with hydrate of potash, although he obtained none when it was heated alone in a tube. By extending his experiments further, he found that many non-nitrogenous organic bodies, as also many metals, presented this phænomenon, as for instance, iron, zinc, tin, lead, arsenic, and also copper. He obtained, for example, a very perceptible quantity of ammonia with woody fibre, oxalate of potash, oxalate of lime, tartrate of lead, acetate of lime and asphaltum; with acetate of potash, acetate and tartrate of lead, tartrate and benzoate of potash, oxalate of lead, sugar, wax, olive oil and naphthaline, very little; and with resin, alcohol, æther and olefiant gas, none whatever. The quantity of ammonia agreed in a remarkable manner with the quantity of hydrate of potash used in the experiment. He further observed, that perfectly pure hydrate of potash, evaporated so far that it ceased to give off water, when heated alone yielded no ammonia, but that it acquired this property when exposed to the air for some time. He observed exactly the same with caustic lime and hydrate of lime, and also with fresh prepared potash-ley allowed to stand for twenty-four hours.

Faraday further obtained ammonia when he heated a strip of well-purified zinc with hydrate of potash made from potassium, in a carefully prepared atmosphere of hydrogen;

but could discover no ammonia when he heated the zinc with hydrate of potash which had been previously kept in a state of fusion until it ceased to give off water. He states, moreover, that the ammonia was generally observed before the disengagement of the hydrogen, by the decomposition of the substance employed, commenced.

Tartrate of lead ignited with potash and the cold residue brought in contact with a drop of water, evolved ammonia.

White clay from Cornwall, which after being strongly ignited was exposed to the air for eight days, yielded much ammonia, while another exactly similar portion of the same clay, which after ignition was preserved in a well-stoppered bottle, gave no ammonia.

Pure sea sand, heated to bright redness in a crucible and cooled on a plate of copper, gave no trace of ammonia, although it was very readily observed when the hot sand previous to its being heated was held for some moments in the hand and stirred about with the finger.

These experiments evidently agree with the observations of Braconnot*, who states that many porous minerals, such as trap from Chaume de Tendon, eurite, some species of granite, serpentine from the Vosges, amphibole, muschelkalk, &c., by distillation in a glass retort, yielded an ammoniacal product.

The experiments of Faraday show with the greatest accuracy that the ammonia was not only not formed, but that it either existed already in the material employed, or received it from the air by exposure. The quantities obtained were so extremely small that he could not estimate them.

In the foregoing experiments I have not only confirmed, but at the same time demonstrated the correctness of Faraday's statement, that the nitrogen of the atmosphere does not in any way possess the property of forming ammonia with hydrogen at the moment of its separation from any combination. If this were the case, a quantity of ammonia capable of being estimated, and in proportion to the duration of the experiment or the quantity of the material, would have been obtained in the experiments with tin, iron and sugar, in which, by the gradual heating of the substance with an alkali in a continued current of air or of nitrogen, the conditions for the formation of ammonia were as favourable as possible throughout the whole combustion; but this did not occur, and by proper care we are even in a condition to avoid every trace of ammonia, although nascent hydrogen may come in contact with nitrogen gas.

If we consider that ammonia forms a never-failing constituent of our atmosphere, that further, it is a body which is easily

* *Annales de Chimie et de Physique*, t. lxvii. p. 104.

absorbed by liquid and porous substances, particularly when these latter possess at the same time the properties of an acid, we must at once perceive that, being in possession of an exceedingly delicate test of the presence of ammonia, that volatile alkali must be found in all, or nearly all, substances exposed to the air.

It is quite evident from this why Faraday did not obtain ammonia with fresh hydrate of potash which had been previously melted, nor with resin which is not a porous body, although resin, like other organic bodies, was decomposed with the disengagement of hydrogen gas by fusion with the hydrate. A small quantity of nitrogen contained in the body as a constituent may be in part or altogether the cause of the disengagement of ammonia in many cases where Faraday observed it. The fact that the flocculent black residue always obtained by the solution of zinc in sulphuric acid after being well washed disengages a pretty considerable quantity of ammonia, accounts very easily for the presence of nitrogen in commercial zinc. Cast iron, according to Schafhaeutl, also contains nitrogen.

The statements contained in most treatises on chemistry, that iron by its change into oxide under the combined influence of moisture and air containing carbonic acid affords the nitrogen of the latter the conditions necessary to form ammonia, agree exactly with the above cases of its supposed formation. This production of ammonia, if it actually took place, presupposes that iron is capable of decomposing water with the disengagement of hydrogen gas at the common temperatures, which is by no means the case; it presupposes further, that the hydrogen on being set free possesses a far greater affinity for the nitrogen than for the oxygen of the atmosphere, which completely contradicts our general experience. At high temperatures, where water would be decomposed by iron, ammonia is not formed. Kuhlman* obtained only hydrogen and nitrogen gases, but no ammonia, by the passage of steam and nitrogen over pyrophorous iron heated to a strong red heat.

I have repeated the doubtful experiment of Austin (at least according to the result of Hall†), in such a manner that the ammonia contained in the atmosphere (but not its carbonic acid) was as perfectly as possible shut out. I introduced into a flask of from 4 to 5 litres capacity, some iron nails (one pound) previously cleaned from all oxide by dilute hydrochloric acid, and then well washed with pure water, and also sufficient distilled water to cover the bottom. The flask was connected air-tight by an intermediate tube with a second smaller one,

* *Abhandlung ueber die Saltpeterbildung*: *Annal. der Chem. und Pharm.*, Bd. xxix. S. 285.

† *Ann. de Chim. et de Phys.* t. ii. p. 42.

which contained a small quantity of very dilute muriatic acid. By a second hole bored in the cork of the small flask, a tube containing asbestus moistened with pure sulphuric acid was attached, and through which the external air communicated with that contained in the greater flask. The object of the hydrochloric acid was to prevent the ammonia formed from passing into the sulphuric acid. The air was renewed every day in such a manner through a second tube closed with wax in the cork of the first flask, that the air entering must pass through the sulphuric acid tube.

After from 14 to 18 days oxidation, the oxide, of which a considerable quantity had already formed, was washed out of the flask with water and a little dilute hydrochloric acid; dissolved in hydrochloric acid and the solution to which chloride of platinum was added, evaporated nearly to dryness in a water-bath. The residue dissolved completely in æther-alcohol, and did not deposit a trace of ammonio-chloride of platinum even after standing for twelve hours, nor could any ammonia be found in the hydrochloric acid contained in the small flask. If the iron was here oxidized at the expense of the water, and if the hydrogen by that means set free had at the moment of its disengagement formed ammonia with the nitrogen of the air, nearly 3 grammes of ammonio-chloride of platinum would have been obtained for every gramme of the oxide treated in the above manner. This is a quantity which could not escape observation.

There is no doubt from this that the ammonia observed in the rust of iron was obtained from the atmosphere.

Herman*, in an essay "On the decay of wood," mentions an experiment in which the nitrogen of the atmosphere was directly absorbed and partially converted into ammonia by the decay of fresh wood. Herman found nearly one-third part of the nitrogen, which according to his experiments existed as a constituent of the wood, in the products of its decay. He concludes from this that two parts escaped in the form of ammonia.

The most perfect process of decay with which we are acquainted is the production of acetic acid from alcohol. If the nitrogen of the atmosphere possessed the property of taking part in these metamorphoses instead of pure acetic acid, an ammoniacal salt of it would be obtained in the quick process for the manufacture of vinegar, where the woody fibre undergoes a slow decay with the alcohol. As yet however no ammonia-formation has been observed.

The process of decay of organic substances which contain little or no nitrogen at the surface of our planet, is as old as

* *Journ. für Prakt. Chemie*, Bd. xxvii. S. 165.

the occurrence of living matter upon it; it is so general and everywhere perceptible that our atmosphere would soon be poisoned with ammonia, there being no such chemical attractions for *nitrogen* gas (as an element) as for oxygen, and its amount of nitrogen would certainly have decreased, if this most indifferent of all gaseous elements possessed the property of contributing as such to the formation of ammonia.

XXXIV. *Examination of Astringent Substances* (continued). *By* John Stenhouse, *Esq.*, *Ph.D.*

Read Februa y 21, 1843.

Black and Green Tea. GREEN and black tea are said by Mulder, the chemist who has most recently examined the subject, to be both derived from plants of the same species. The differences observable in them are, as he alleges, chiefly owing to their being collected at different periods of their growth, and to the greater or less degree of heat with which they are subsequently dried; the black teas being strongly heated upon iron plates, while the green teas are exposed to a comparatively moderate temperature. If this statement is correct, it may serve to explain what has been long observed, that an aqueous infusion of black tea, though quite transparent while hot, becomes muddy on cooling, while an infusion of green tea retains its transparency even when quite cold. The reason of this difference probably is, that most of the essential oil of black tea is converted, by the partial roasting it has undergone, into a resinous matter, which though soluble in hot is nearly insoluble in cold water, while the essential oil of green tea, on the contrary, remains nearly unchanged, which is probably the cause both of the clearness of its solution and perhaps also of the more powerful effect which green tea is well known to exert on the animal œconomy.

The aqueous infusion of both green and black tea give dull olive-black precipitates with protosulphate of iron, which on standing become leaden black. Infusions of tea also, when evaporated to dryness and distilled, give crystals of theine which collect on the sides and neck of the retort, while the empyreumatic liquor which passes into the receiver gives pretty distinct indications of containing pyrogallic acid.

The Tannin of Tea.—In order to separate the tannin of tea from the other proximate principles of the plant, its aqueous infusion was precipitated with acetate of lead, and the precipitate carefully washed with hot water. Green tea gave a

bright yellow precipitate, but that of black tea had a brownish-yellow colour. The lead salts were decomposed by sulphuretted hydrogen: the solution of the tannin of green tea had only a slight yellow colour, while that of black tea had a much darker colour, but in other respects the properties of both appeared to be the same. The following are the effects upon them of different reagents:—with solution of gelatine they gave white bulky precipitates, and they also gave copious white precipitates with tartar-emetic. Protosulphate of iron throws down bright bluish-black precipitates, nitrate and chloride of iron, olive black, and acetate of iron purple black precipitates. The solution of the tannin when evaporated to dryness on the water-bath, became of a reddish-brown colour, and was partially decomposed.

When this tannin was subjected to distillation, it invariably yielded a quantity of pyrogallic acid, which sometimes appeared in crystals upon the sides of the retort, but which more frequently remained dissolved in the empyreumatic liquor which passed into the receiver. In this it was easily detected by the usual reagents. It gave a fine reddish-purple colour when dropped on milk of lime, with protosulphate and protonitrate of iron, a fine indigo-blue colour, and with protochloride, a blue resembling ammoniuret of copper. As the quantity of pyrogallic acid obtained was always much less than that which the same quantity of the tannin of either galls or shumac would have yielded, I was led to suspect that it did not arise from the decomposition of the tannin in the tea, but resulted from some gallic acid with which the tannin was mixed. Of the accuracy of this opinion I was speedily convinced by the following experiment:—On treating a strong solution of the tannin with nearly half its bulk of sulphuric acid added by little and little at a time, a dark brown precipitate fell consisting of the tannin combined with the acid. It was however much more soluble than the corresponding compound of the tannin of galls. It was collected on a cloth filter, strongly compressed, and washed with a little cold water to free it as much as possible from adhering acid. When subjected to distillation it did not afford the slightest trace of pyrogallic acid, showing evidently that the pyrogallic acid I had previously obtained was not derived from the tannin of the tea. When another portion of the precipitated tannin was boiled with tolerably dilute sulphuric acid, it did not yield any gallic acid, but was changed into a dark brown substance, nearly insoluble in cold, and but very little more so in boiling water. It gave a grayish black precipitate with protosulphate of iron, but was not precipitated either by gelatine or tartar-

emetic. It dissolved however pretty easily both in alcohol and alkalies, forming dark brown solutions. It is evident therefore that though in some of its properties the tannin of tea agrees pretty closely with that of nut-galls, still the products of its decomposition are essentially different.

The tea was next examined for the gallic acid which it evidently contained, and this I was always able to procure by either of the following methods:—The mixture of tannate and gallate of lead obtained by precipitating a decoction of tea by acetate of lead, was decomposed as before by sulphuretted hydrogen and evaporated to dryness. It was then macerated with a very little cold water which removed most of the tannin, but dissolved scarcely any of the gallic acid. The residue was again dried, reduced to powder and mixed with some sand, was repeatedly agitated with æther in a stoppered bottle. The æthereal solution was then poured off, and almost the whole of the æther was recovered by distillation. The residue when left to spontaneous evaporation deposited crystals, which at first had a yellow colour, but which were rendered perfectly white by a second crystallization. The other process was somewhat more tedious, but by it very small quantities indeed of gallic acid can be detected. It consists in putting a number of bits of prepared skin into the mixed solution of tannin and gallic acid already mentioned, and allowing them to remain for nearly a fortnight till the whole of the tannin is absorbed by the skin. The gallic acid is then precipitated by acetate of lead, and the precipitate having been well washed, first with hot water and then with spirits of wine, is to be decomposed by sulphuretted hydrogen.

When evaporated to dryness and treated with æther as before, crystals of gallic acid are readily obtained, which are at first much purer than those got by the former method. I examined several specimens both of black and green tea, and also one of Assam tea, in every instance with similar results. It is evident, therefore, that tea, besides a species of tannin which gives bluish-black precipitates with protosulphate of iron, invariably contains a small but constant quantity of gallic acid, a constituent which has hitherto been overlooked.

Myrobalans.—The name Myrobalans is applied to the fruit of several East Indian trees, the species of which are, I believe, not yet all accurately determined. That which I examined was the yellow kind, the fruit of the *Jerminalia Chebula*. The ripe fruit has a brownish-yellow colour, is pear-shaped, and deeply wrinkled. It consists of a white pentangular nut containing a small white oily kernel, and is covered

by a mucilaginous and very astringent husk, nearly two lines in thickness. Each of the fruit weighs from 70 to 100 grains, and of this 50 or 60 grains are husk. It is in the husk that the whole of the astringent matter is contained, and it may be easily separated from the nut by slightly pounding or bruising the fruit. The powder of the husk is dark yellow, and its taste is very sharp and astringent. The colour of its aqueous infusion is deep yellow. With protosulphate of iron it gives a deep bluish-black precipitate, which is rather deficient in lustre. The dullness of the colour is owing to the presence of impurities in the husk, for on purifying the astringent matter by precipitating it with acetate of lead, and then decomposing the lead compound with sulphuretted hydrogen, the solution thus obtained gives as fine a colour as can be procured from infusion of galls. With gelatine it gives a very copious, slightly yellow precipitate, the quantity of astringent matter contained in myrobalans being very considerable. With tartar-emetic it also gives a copious brownish-yellow precipitate. With protonitrate and protochloride of iron, it gave bluish-black precipitates, which soon changed to olive-black, and with acetate of iron, a fine purple-black precipitate. When the decoction of myrobalans is evaporated to dryness and distilled, it yields abundance of pyrogallic acid; this I found, however, to be derived, not from the decomposition of the tannin it contains, but from a quantity of ready-formed gallic acid. Sulphuric acid occasions a very scanty dark brown precipitate in the infusions of myrobalans, if at all dilute, as the combination which this tannin forms with sulphuric acid is pretty soluble. From concentrated solutions, the tannin is readily precipitated as a yellowish-brown tenacious mass. Having been collected on a cloth filter, and freed as much as possible from adhering acid, it was dried and distilled. It yielded no pyrogallic acid, and scarcely any empyreumatic oil; another portion of the same tannin, though boiled in dilute sulphuric acid, was not converted into gallic acid, but changed into a dark insoluble mass.

Gallic acid may be readily obtained from myrobalans by precipitating its decoction with a solution of glue, filtering and evaporating to dryness. On treating the residue with æther, pouring off the solution, recovering the greater portion of the æther by distillation, and leaving the remainder to spontaneous evaporation, crystals of gallic acid were deposited in a few hours. The quantity of gallic acid in myrobalans is pretty considerable.

Besides tannin and gallic acid, myrobalans contains a good deal of mucilage, and a brownish-yellow colouring matter,

which Dr. Bancroft states was employed in India in his time as a yellow dye. Myrobalans have long been employed by the calico-printers of India instead of galls, and from the large quantity of astringent matter they contain, I think perhaps they might be worth the attention of the tanners and calico-printers of this country. A decoction of myrobalans makes a very tolerable ink, which however, as we have already stated, is rather deficient in lustre.

Bistort, Polygonum Bistortus.—The root of this plant, which is pretty common in Scotland, has a pale pink colour internally, but when it is exposed to the air for some time it becomes deep yellow. Its aqueous solution is yellowish at first, but on standing it assumes a fine red colour, and the same effect is immediately produced by boiling it with any of the alkalies. With protosulphate of iron it gives a bluish-black precipitate, a good deal resembling that of galls, but having a bluish-purple shade. Gelatine produces a copious brownish precipitate in a solution of bistort, which shows that the quantity of astringent matter it contains is considerable. With tartar-emetic it gives a brownish-white precipitate. When extract of bistort is evaporated to dryness and distilled, it gives distinct indications of pyrogallic acid. The pyrogallic acid however, as in the case of myrobalans, was derived not from the tannin in bistort, but from a quantity of gallic acid with which it was mixed, for on precipitating the tannin by sulphuric acid, and distilling it alone, not a trace of pyrogallic acid was obtained, and when boiled with sulphuric acid it was not converted into gallic acid.

The gallic acid it contains was easily obtained from bistort by precisely the same process as that already described. Its quantity, compared with that of the tannin in the root, was very considerable.

Besides tannin and gallic acid, bistort contains a brownish-red colouring matter, and a quantity of mucilage. Bistort may likewise be made to furnish a very tolerable ink, which appears to stand very well. It has a bluish-purple shade, owing to the reddish colouring matter of the root.

The Cashew Nut.—The outer rind of the Cashew nut, the fruit of the *Anacardium longifolium*, contains a considerable quantity of a species of tannin which gives bluish-black precipitates with the sulphate, nitrate and chloride of iron, and a bluish-purple precipitate with the acetate. It is also readily precipitated by gelatine, but not by tartar-emetic. This tannin is mixed with a small quantity of gallic acid. The shell of the fruit also contains a good deal of a fatty matter, which is solid at ordinary temperatures and crystallizable. It is easily

saponified when boiled with an alkali, its compound with soda crystallizes in large scales. This fat contains an acrid substance which vesiccates, but it contains no sulphur. When the fat is first expressed from the nut it is but slightly coloured, but by exposure to the air it becomes first brown and then black, and loses much of its acrimony.

Pomegranate Rind.—The rind of the pomegranate contains a considerable quantity of a species of tannin which precipitates gelatine copiously, but gives only a very feeble precipitate with tartar-emetic; with protosulphate, chloride and nitrate of iron, it gives precipitates which are at first deep blue but almost immedately change to very dark olive. With acetate of iron it gives a purple precipitate. Reuss, who has made an analysis of pomegranate rind, states that he found it to contain a little gallic acid. I have been unable to find any, though I have sought it very carefully.

Larch Bark.—The bark of the larch is employed in Scotland to some extent in tanning. The quantity of tannin it contains is considerable, but the leather made with it is of inferior quality. The aqueous solution of the bark is strongly acid to test paper, and has at first a pale yellow colour, which exposure to the air renders brownish-red; it gives a copious fawn-coloured precipitate with gelatine, but none with tartar-emetic. With the sulphate, chloride and nitrate of iron, it gives olive-green precipitates. Acetate of iron throws it down of a bluish-purple colour. Sulphuric acid precipitates it of a reddish-yellow colour. When boiled with the acid it dissolves, and the liquid assumes a fine scarlet colour like the infusion of Brazil wood. The altered tannin precipitates on cooling in beautiful red flocks, as it is but little soluble in cold water. It is very soluble in alcohol and alkalies, and its solutions have a rich scarlet colour, which is the most characteristic reaction of this species of tannin. Larch bark also contains a good deal of mucilage and resinous matter. Birch bark, alder bark, and tormentil root, contain all of them considerable quantities of tannin, which closely resemble that of larch bark. All these species of tannin are readily precipitated by gelatine, but not by tartar-emetic. They give olive-green precipitates with most of the salts of iron except the acetate, which throws them down of a bluish-purple colour, which on standing changes to a leaden gray. When boiled with alkalies they immediately assume a fine red colour, but they differ from the tannin of the larch in not being reddened by sulphuric acid. I think it unnecessary to go into more minute details respecting them, as I have been unable to derive from them any determinate or crystalline compounds. I

shall leave this subject, therefore, for the present with one or two general observations.

The great difficulty of examining the different species of tannin with a view to classifying them, is chiefly owing to their amorphous nature, to the great similarity of their properties, and to the circumstance, that except in the case of nut-galls and shumac, the products of their decomposition are of a very indeterminate character. We think however that there are good grounds for believing that both nut-galls and shumac contain the same species of tannin, for the effects of reagents upon it are exactly the same, and the products of its decomposition, when boiled with either sulphuric or muriatic acid, when destructively distilled, or when left to spontaneous decomposition, are in every instance identical, from whichever of these sources it has been derived. It is remarkable also that in so many instances, in eight cases out of ten which I have examined, the species of tannin which give bluish-black precipitates with protosulphate of iron are accompanied with larger or smaller quantities of gallic acid. In the present state of our knowledge it is impossible to say whether the gallic acid has originally existed in these substances, or has resulted from the decomposition of the tannin they contain. In the case of galls and shumac the latter opinion is probable enough, as we are easily able to effect this change by artificial means, and it also, as is well known, occurs spontaneously. In the case of the other species of tannin, however, we are still unacquainted with any instance of a similar transformation. It is to be hoped that subsequent researches may yet throw light on this very obscure subject. It is also rather singular that in the case of some of those species of tannin which give green precipitates with salts of iron, a somewhat similar circumstance occurs. Thus the tannin of catechu is accompanied by a crystalline acid body, catechine, which also gives green precipitates with salts of iron. I have likewise observed that in the case of infusions of birch bark, alder bark, &c., when the whole of the tannin they contain had been removed by gelatine, the clear liquid when filtered still contained a substance which precipitated salts of iron olive-green, just as the tannin had done, and which threw down salts of lead as copious dark yellow precipitates. When the lead salts were decomposed by sulphuretted hydrogen, I obtained an amorphous acid substance of a bright yellow colour, which was soluble in water, alcohol and æther, but which did not appear to be crystallizable.

XXXV. *On Theine and its Preparation.*

By John Stenhouse, *Esq.*, *Ph.D.*

Read March 21, 1843.

THE process which I have found most suitable for preparing theine, is both easy and productive, and is simply as follows:—A decoction of tea is first treated with a slight excess of acetate of lead, which throws down the tannin, and almost all the colouring matters it contains. It is filtered while hot, and the clear liquor is evaporated to dryness. It forms a dark yellowish mass, which is to be intimately mixed with a quantity of sand, and introduced into Dr. Mohr's subliming apparatus. This should then be set upon a sand-bath, or still better on a metallic bath, and a moderate heat applied to it for 10 or 12 hours. The theine sublimes in beautifully white, anhydrous crystals, and is deposited upon the paper diaphragm which runs across the apparatus. The only thing to be observed is, that the temperature should never rise too high, as the more slowly the operation is conducted, the finer are the crystals and the greater is their quantity. The following are the results obtained by this process in four different trials.

I. One pound of green Hyson tea gave 72 grains of perfectly white theine, and 2 grains which were slightly coloured, in all 74 grains = 1·05 per cent.

II. 8 oz. of black Congo tea gave 34·5 grains pure theine, and 1·5 grains impure, in all 36 grains = 1·02 per cent.

III. 6 oz. black Assam tea yielded 36 grains theine = 1·37 per cent.

IV. 1 lb. of a cheap green tea called Twankay, gave 69 grains = 0·98 per cent. This last was sublimed too quickly, or it would probably have given a little more theine.

We have four determinations of the theine in different specimens of tea by Mûlder. He found in Chinese Hyson 0·43 per cent. theine, in congo 0·46 per cent, in Japanese Hyson 0·60 per cent., and in Japanese Congo 0·65 per cent.

Mûlder's process consisted in boiling the filtered decoction of the tea with magnesia, evaporating to dryness and then dissolving out the theine from the dry mass with æther. I have repeatedly tried his process, but found it very troublesome and unproductive; besides, the theine always requires more than one crystallization to render it quite pure, and the high price of æther, in Great Britain, at least, is a very serious inconvenience. It is to the presence of theine, I believe, that the bitter taste of tea is chiefly owing, and a tolerably correct idea of the quantity of theine in any specimen of tea may be formed from the degree of bitterness which it exhibits. The Assam tea, which yielded such a large proportion of theine,

was remarkably bitter, but it appeared rather deficient in essential oil.

Theine may also easily be made from coffee, by a slight alteration of the method just described; the coffee beans should not be roasted, as this would drive off much of the theine, but only slightly dried, and then ground or pounded, and repeatedly boiled with water till exhausted. The filtered decoction should first be precipitated while hot with basic acetate of lead. It should then be filtered and boiled with a little hydrated oxide of lead, which occasions a further precipitate, which is also to be separated by filtration. The clear liquor is to be evaporated to dryness, and sublimed exactly in the same way as the extract of tea. From a pound of coffee, in the course of several trials, I obtained from 12 to 18 grains of theine, which was sometimes not so perfectly white as that made from tea, as it was accompanied by a little more empyreumatic oil. It was easily rendered perfectly pure with scarcely any loss, by subliming it a second time at a very moderate temperature. A considerable quantity of theine may be easily made by sublimation, from either tea or coffee, in the course of two days, while the ordinary way of procuring it is both tedious and expensive.

Several chemists have been induced to affirm that none of the beneficial effects which tea and coffee produced on the animal œconomy, should be ascribed to the theine they contain, owing to the smallness of the quantity in which they supposed it to exist in these substances. Professor Liebig has, as is well known, recently advanced the very opposite opinion, and has rendered it highly probable that theine will yet be found to possess valuable medical properties. I hope that some medical practitioners may soon be induced to try if its utility in medicine will be found equal to the expectations which have been formed of it.

In reference to the sublimation of theine, I may mention that I have found it advantageous to make a slight addition to Dr. Mohr's subliming apparatus, described in a previous paper. Instead of pasting the diaphragm of bibulous paper immediately on the rim of the iron pan, I paste it on a moveable rim of tin plate about an inch deep, which goes close round the outside of the pan, and which projects about one-eighth of an inch within it. When covered with the paper it exactly resembles a small sieve, and may be easily removed and replaced at pleasure. This enables us to stir the mass we may be subliming from time to time, and thus to heat the whole of it more equally. Now this could not be done in the usual apparatus without destroying the diaphragm.

Theine in Paraguay Tea.—I am indebted to the kindness of Professor Christison for a quantity of Paraguay tea, or "yerba mate," as it is called. It consists of the leaves and small branches of the *Ilex paraguayensis*, which after being strongly roasted, have been reduced to a coarse powder. This substance is extensively used in South America as a substitute for tea. Its taste is very bitter, partly resembling that of ordinary tea, but also approaching somewhat to that of sumach. Its reactions were studied a number of years ago by Professor Tromsdorff, and are pretty fully stated in the eighteenth volume of the *Annalen der Pharmacie*, page 90. As my own observations coincide pretty closely with his, it appears unnecessary to give a detailed account of them. In proceeding to examine Paraguay tea for theine, acetate of lead was added to its decoction, which threw down a very dense greenish-yellow precipitate, and when this was removed by filtration, subacetate of lead also produced a considerable quantity of a bright yellow precipitate. The clear liquid when drawn off and evaporated to dryness, left a good deal of a tenacious dark brown mass, which was very hygroscopic. When a little of it was subjected to distillation, a quantity of long flat crystals, exactly resembling the theine, sublimed into the sides and neck of the retort; and at the same time the very peculiar pungent smell which theine always emits when subliming became very perceptible.

The remainder of the brownish-yellow substances already mentioned was reduced to fine powder, and intimately mixed with a large quantity of sand to prevent its agglutinating. It was then repeatedly agitated with æther in a stoppered bottle. The æthereal solution when poured off and distilled pretty low, deposited a quantity of crystals which were slightly coloured at first, but which were rendered perfectly white by repeated crystallizations. In their crystalline form, taste, solubility in water, alcohol and æther, and in all their reactions, they correspond exactly with ordinary theine. I may mention also, as an additional confirmation of the truth of this opinion, that in the course of some experiments upon theine, I have found an excellent test for that substance, by which its presence even in small quantities may be readily detected. It consists in the action of nitric acid upon theine, the effects of which are very different according to the quantity of the acid employed, and the length of time during which its action is continued. If theine is boiled for a few minutes with only twice or thrice its weight of fuming nitric acid, nitrous gas is given off in abundance, and a bright yellow solution is obtained. If a little of this liquid is taken out and

gently evaporated to dryness in a porcelain basin, it leaves a deep yellow mass. If a drop of ammonia is then let fall upon it and a gentle heat is applied, a bright purple colour is immediately produced, which cannot be distinguished by the eye from that obtained from uric acid when similarly heated. This rich purple colour is permanent, its aqueous solution has a deep crimson shade. It also dissolves in spirits of wine, but it is not soluble in æther. Its colour is immediately destroyed by a solution of potash, which does not change it to an indigo-blue, as it does murexide. The substance which gives the red colour with ammonia does not appear to be crystallizable.

Now as I obtained the purple colour as readily from theine prepared from Paraguay tea as from that made from ordinary tea and coffee, I have not the least doubt that they are both identical substances. Unfortunately, from the smallness of the quantity of Paraguay tea in my possession, I have not been able to procure more than a few grains of the theine in a state of purity, and have been prevented therefore for the present from subjecting it to analysis. This however I have good reason to believe I shall be able to do in the course of a few weeks.

The quantity of theine in Paraguay tea is by no means great, but no doubt much of what it originally contained had been destroyed by the injudicious way in which it is manufactured in Paraguay. The branches of the yerba tree are there cut down and spread upon a sort of wooden barbacue, under which large fires are kept burning. The yerba is therefore exposed to a very high temperature, and as theine sublimes pretty readily, it is plain that a good deal of it will necessarily be dissipated.

It is somewhat singular, as Professor Liebig has observed, that the other three vegetable substances which are known to contain theine, tea, coffee, and guarana, though derived from plants of very different natural families, are all of them extensively employed as refreshing beverages. The circumstance that Paraguay tea, which is extensively applied to precisely the same purpose, also contains theine, is calculated, I should think, to give additional probability to the views of Professor Liebig on this subject.

It is not unlikely that theine will soon be found to occur in other vegetables besides those in which it is already known. The easiest way perhaps to examine a plant for theine, which can be done in the course of a few hours, is to precipitate its infusion with subacetate of lead, to filter and evaporate the clear liquid to dryness. If a portion of the matter thus ob-

tained be distilled, any theine it may contain will be immediately deposited in long flat crystals on the neck and sides of the retort.

Chamellia Japonica.—Through the kindness of Professor Balfour I was enabled to examine a quantity of the leaves of the *Chamellia Japonica*, a plant whose botanical characters approach very closely those of Tea Bohea. I found that the Chamellia does not contain any theine, and indeed its chemical properties have very little resemblance to those of the tea plant. It has scarcely any of the bitter astringent taste by which both green and black tea are distinguished, and it appears wholly devoid of any essential oil. It contains, however, a small quantity of tannin, which gives olive-green precipitates with salts of iron, and very copious yellow precipitates with acetate of lead. It occasions a very slight precipitate only in a solution of gelatine, and does not precipitate tartar-emetic at all.

Besides tannin the Chamellia also contains a quantity of mucilage, some chlorophyle, and a waxy resinous matter.

I have also examined the holly, the *Ilex Aquifolium*, for theine, but without success. Its chemical properties appeared pretty similar to those of the *Chamellia Japonica*.

Action of Nitric Acid upon Theine.—As has been already mentioned, when theine is boiled with three or four times its weight of strong nitric acid, it is converted with copious evolution of nitrous gas into a deep yellow liquid, which when gently evaporated to dryness and slightly warmed, gives with ammonia a purple colour similar to that of murexide. This we have also mentioned is an excellent test for theine, and it forms a very pretty class experiment. The yellow liquid contains a very soluble crystalline body, which, when most of the nitric acid has been driven off, and the solution evaporated nearly to a syrup, crystallizes in long, hard, colourless needles. They have a rather sweetish taste, and when freed from adhering acid by repeated crystallizations, appear to be neutral to test paper, or at least only very slightly acid. Both this and the red colouring matter, however, appear to be the products of the imperfect oxidation of the theine. If the theine is boiled for some hours in a great excess of nitric acid till a drop of the solution, when evaporated to dryness, is no longer yellow but white, the addition of ammonia does not produce any change of colour whatever. Both the yellow liquid and the substance which crystallizes in needles are then found to have disappeared. If the greater portion of the nitric acid is distilled off, and the liquor concentrated to a syrup as before, it readily concretes on cooling into a mass, containing a num-

ber of large shining crystals. The mother-liquor which surrounds them appears to consist chiefly of very deliquescent ammoniacal salts. The crystals have a sweetish taste, grate between the teeth, and have a bright silvery lustre. Their crystalline form is not at all distinct, but they form large plates which readily crystallize. They dissolve in about three times their weight of cold water, but in a much smaller portion of hot water. They are readily soluble also in alcohol and æther. Their great solubility renders it a little difficult to purify them. The best way of doing so is by repeatedly crystallizing them out of water, and by pressing them between the folds of blotting-paper. When purified they are neutral, or at least redden litmus paper very feebly. The smallest portion of an alkali when added to their solution renders it alkaline. When heated they readily sublime, and are deposited in fine shining crystals on any cold object. They take fire easily and burn with a bright flame. They do not give off ammonia when heated with potash.

They occasion no precipitate or change of colour in solutions of nitrate of silver, acetate of lead, or sulphate of iron.

I hope soon to subjoin the results of their analysis, with a more minute account of their properties.

5th. Two lbs. of coarse black bohea tea, such as usually sells for three shillings a pound, gave 99·5 grs. theine = 0·70 per cent.

Analysis of the sublimed Theine.—0·285 substance gave 0·5125 carbonic acid, and 0·132 water =

		Calculated Number.
Carbon ...	49·72	49·79
Hydrogen	5·14	5·08

Analysis of Theine from Paraguay Tea.—0·2905 dried at 212° gave 0·525 carbonic acid, and 0·1345 water =

		Calculated Number.
Carbon ...	49·96	49·79
Hydrogen	5·145	5·08

The want of material unfortunately prevented me from determining the nitrogen also.

Hydrochlorate of theine forms a double salt with chloride of platinum. It may be easily obtained in small but very distinct orange-coloured crystals by adding chloride of platinum to a hot solution of theine in hydrochloric acid. In a few minutes as the liquor cools the crystals begin to form, and gradually subside as a mass to the bottom of the vessel. When dried at 212° and burnt,

			Per cent.	Calculated Number.
I.	0·461 grs. salt gave	0·112 of platinum	= 24·29	... 24·48
II.	0·529 ...	0·130 ...	= 24·57	
III.	0·5828 ...	0·143 ...	= 24·53	
IV.	0·458 ...	0·112 ...	= 24·45	

These numbers lead to the rational formula $C^{16}\ H^{10}\ N^4\ O^4\ H\ Cl + Pt\ Cl^2$, which gives 24·48 per cent. platinum, and double the ordinary atomic weight of theine.

Atoms.			Per cent.
16	C	= 1222·960	
10	H	= 124·795	
4	N	= 708·160	
4	O	= 400·000	
1	H Cl	= 455·140	
2	Cl	= 885·300	
1	Pl	= 1233·26	= 24·48
		5029·615	

The salt employed for the two first determinations was washed with alcohol, and that for the two last with æther. This double salt appears therefore much more stable than the hydrochlorate of theine. I am proceeding to determine the quantity of its other constituents.

XXXVI. *On the Constitution of the Subsalts of Copper.*—No. I. *On the Subsulphates.* *By* J. Denham Smith, *Esq.*

Read April 4, 1843.

THE results of several analyses of some of the basic salts of copper made at a former period not agreeing with the constitution ascribed in many instances to these compounds, again directed my attention to their composition, and further experience has confirmed this disagreement, showing either that the analytic results are in one case incorrect, or that the composition of these salts, prepared at various times by the same method, is not constant.

The mode adopted for determining the composition of the subsulphates of copper, was to dissolve one portion of the salt in pure hydrochloric acid, and ascertain the quantity of sulphuric acid by a salt of barytes. To estimate the proportion of black oxide of copper, the course pursued in the experiments alluded to, was solution of another portion of the salt, under examination, in dilute sulphuric acid and precipitation by a caustic alkali from the boiling solution, carefully washing, ig-

niting, and weighing the precipitate. This mode, however, is open to the objection of the possible adherence of portions of the precipitant, or other foreign matter, to the oxide; and as I subsequently found that this class of salts when exposed to a lengthened and bright ignition, care being taken not to fuse the oxide, loses the whole of its sulphuric acid, I adopted this latter mode of estimating the oxide, it being one which appears to me free from objection: I would remark that the residual oxide after this ignition was always examined for sulphuric acid, and if any was detected the experiment was rejected. The deficiency of weight between that of the salt operated on and the sum of the sulphuric acid and oxide of copper, was estimated as water.

This method of estimating the water may be objected to as an indirect one, but I consider it more likely to be correct, where a substance possesses so simple a composition as in the case of these subsulphates, than any mode would be that could be devised of actually obtaining and weighing the water; especially as these salts were thoroughly washed until no soluble matter could be detected in the washings, and dried either in a water-bath or on a porous stone, and exposure to the atmosphere at the temperature of the laboratory, 50° to 80° Fahr.

In those instances where the results of my analyses were not in accordance with those cited by Berzelius, Graham, Kane, Thomson and others, the examination was at times repeated, sometimes thrice, and the mean of these analyses taken in estimating the composition of the salt. The modes of preparation and the constitution of these salts I shall classify in the order of their composition, and at the same time notice discrepancies, when such occur, between my results and those of the analysts who have preceded me.

Trisulphate of Copper.—By boiling an equivalent of oxide of zinc and two equivalents of sulphate of copper together, the subsulphate noticed by Berthollet, of a bright green colour with a shade of blue, is obtained. The mean of two analyses gave, from 50 grs. of this salt, 33·97 grs. of sulphate barytes and 34·3 grs. of oxide of copper. The composition deduced from these results would seem to indicate the formula $2SO_3\ 6CuO,\ 3HO$; but I am inclined to consider this salt as really consisting of $SO_3\ 3CuO,\ 2HO$, a constitution almost exactly borne out by the second of these analyses, agreeing more nearly with Brunner's analysis of the subsulphate obtained in this way, and also with the composition of some subsulphates prepared in a different manner, but which indicate the composition $SO_3\ 3CuO,\ 2HO$, which will give—

	Theory.	Experiment.
Sulphuric acid . . .	11·24	11·65
Oxide of copper . . .	33·72	34·30
Water	5·04	4·05
	50·00	50·00

By precipitating 250 grs. of crystallized sulphate of copper with excess of potash, washing the brownish-black precipitate with hot water until free from alkali, and boiling this with 250 grs. of sulphate of copper, a light green-coloured powder was produced, the boiling and digestion were continued for forty-eight hours, and the liquor was then evaporated to dryness. The mass was treated with water to dissolve out uncombined sulphate, and washed until free from soluble matter; this when dried gave a pale green powder weighing 172 grs.: of this—

36·32 grs. gave 23·8 grs. of sulphate barytes = 7·35 of sulphuric acid in 32·52 grs., which quantities afforded by ignition 21·56 grs. of oxide of copper; this indicates the formula SO_3 3CuO, 2HO, or 32·52 grs. consist of

	Theory.	Experiment.
Sulphuric acid . . .	7·31	7·35
Oxide of copper . . .	21·94	21·56
Water	3·29	3·61
	32·52	32·52

This salt is also obtained when less than an equivalent of oxide of copper is boiled with an equivalent of sulphate of copper.

In Dr. Kane's tabular view of the sulphates of copper (Transactions of the Royal Irish Academy, &c., vol. xix.), this salt, the trisulphate of copper, is not noticed; but Berzelius has described one, assigning to it 3 equivalents of water. If such a salt exists I have been unable to obtain it; and although I admit that such a composition is by no means improbable, seeing that another subsulphate exists in which the number of equivalents of water and oxide of copper are equal, I am inclined to consider that the third equivalent of water in Berzelius's salt was hygrometric, as in no one instance, although this salt was prepared at several distinct periods and in the mode described by Berzelius, did I obtain results indicating an approximation to the constitution SO_3 CuO, 3HO.

The composition I have assigned to this salt agreed with that quoted by Dr. Thomson, as arrived at by Brunner from the analysis of the subsulphate prepared by Berthollet's process.

Tetrasulphate of Copper.—This salt is obtainable in a great variety of ways. It is precipitated when a cold solution of

sulphate of copper is mixed with an insufficient quantity of carbonate or of caustic soda, or potash to completely decompose it. It may be prepared by digesting together cold,—equivalents of sulphate of copper, and of well washed precipitated oxide of copper; by adding a solution of potash to a warm solution of sulphate of copper until a greenish-blue precipitate falls, and no copper remains in solution; by treating a cold solution in the same manner; by acting on the ammoniacal sulphate by a large quantity of water, &c. Numerous analyses of this salt, prepared by the various processes above mentioned, have only served to confirm the correctness of the formula, SO_3 4CuO, 4HO, assigned to it by Professor Graham and Dr. Kane; it is therefore useless to quote any of these results.

Dr. Kane, in the paper before mentioned, states that "this salt when heated does not lose water until the temperature rises above 300° Fahr., but then loses all." I find, however, by exposing this salt to a temperature of 400°—470° Fahr., that it assumes a grass-green colour accompanied with the evolution of water.

When 43·2 grs. of the dingy greenish-blue powder, obtained by digesting an equivalent of precipitated oxide of copper with an equivalent of sulphate in the cold, were exposed to the above temperature, it changed to a decided green colour and lost 1·63 grs., this is equal to 8·9 grs. of water from 236, the equivalent number of the tetrasulphate of copper, which indicates SO_3 4CuO, 3HO as the constitution of this green subsulphate.

27·07 grs. of the blue subsulphate became of a grass-green colour and lost 1·04 gr. of water, equivalent to 9·07 grs. from 236 grs., and indicating the formula SO_3 4CuO, 3HO as the constitution of this green subsulphate, arising from the loss of an equivalent of water by the blue subsulphate, SO_3 4CuO, 4HO. This green salt on analysis gave from 13·43 grs. 9·4 grs. of black oxide of copper, and 6·05 grs. of sulphate barytes from 11·62 grs., proving its composition to be as above stated, SO_3 4CuO, 3HO, or,

	Theory.	Experiment.
Sulphuric acid . . .	2·37	2·4
Oxide of copper . . .	9·47	9·4
Water	1·59	1·63
	13·43	13·43

This salt is similar to that analysed by Brunner, obtained by boiling equivalents of sulphate of copper and sulphate of potash together, until after repeated washings and boiling no sulphuric acid could be detected in the solution.

When this green salt is moistened, or even boiled with water, it does not change colour, nor re-combine with the equivalent of water it had lost, as I had anticipated from the statement of Dr. Kane, that "at a temperature above 300° it loses all its water, and the brown powder, if exposed to the air, re-absorbs water slowly; if moistened it combines with the water, rapidly evolving heat, and regains its original proportion, and also its proper colour."

There exists another hydrate of the tetrasulphate, obtained by precipitating a very dilute solution of sulphate of copper by a solution of potash, also much diluted, adding the alkali until the supernatant fluid restored reddened litmus to blue; this when dried was an extremely light powder of a very pale blue colour, altogether differing in appearance to the other tetrasulphates; 18·63 grs. of this salt gave 8·28 grs. of sulphate of barytes, and 29·38 grs. afforded 19·33 grs. of black oxide of copper, indicating the formula SO_3 4CuO, 5HO, or

	Theory.	Experiment.
Sulphuric acid . . .	4·79	4·51
Oxide of copper . .	19·19	19·33
Water	5·40	5·54
	29·38	29·38

Pentasulphate of Copper.—This salt is obtained when potash is added to a solution of sulphate of copper, until the alkali is slightly in excess and a light blue-coloured precipitate is obtained; this, unless rapidly washed, becomes gradually dingy, and finally turns to a dark greenish-black colour, probably owing to the loss of combined water. This change often takes place, entirely or partially, during the drying of the precipitate, even when dried by exposure to air, without artificial heat; when obtained free from this blackening effect it is a light powder of a blue colour, a more decided tint than that of the tetrasulphate with five equivalents of water; upon analysis, which was frequently repeated, the constitution of this salt was found to be SO_3 5CuO, 6HO. The results of two analyses of this salt, prepared at different times, are subjoined: 32·2 grs. of the salt gave 21·6 grs. of oxide of copper, and 22·36 grs. gave 9·74 grs. of sulphate barytes, or

	Theory.	Experiment.
Sulphuric acid . . .	4·38	4·83
Oxide of copper . .	21·90	21·60
Water	5·92	5·77
	32·20	32·20

24·3 grs. gave 16·47 oxide copper, and 17 grs. gave 6·52 grs. sulphate of barytes, equal to

	Theory.	Experiment.
Sulphuric acid . . .	3·31	3·2
Oxide of copper . .	16·53	16·47
Water	4·46	4·63
	24·30	24·30

32·2 grs. heated on a sand-bath until it assumed an olive-green tint lost 2· grs., and 36·13 lost 2·2 grs. of water, equivalent to 2 equivalents of water from 294, the equivalent number of the pentasulphate of copper, SO_3 5CuO, 6HO, thus altering its constitution to the formula SO_3 5CuO, 4HO. Besides the subsulphates of copper already described, two others are stated to exist, a disulphate and an octosulphate of copper. Dr. Thomson describes the first, the disulphate, as produced "when crystals of the blue sulphate are dissolved in water and the solution boiled for a long time with a quantity of black oxide of copper, equal to that contained in the salt," and states it to consist of SO_3 2CuO, but gives no water as a constituent of it. L. Gmelin, on Thomson's authority, directs that equal equivalents of the sulphate and oxide of this metal be digested together for some months to obtain the green disulphate. I tried both these plans; by boiling, at various intervals during ten weeks, equivalents of sulphate and oxide, I obtained the trisulphate of copper, SO_3 3CuO, 2HO, a green-coloured powder; by digesting an equivalent of each for thirteen weeks the tetrasulphate, SO_3 4CuO, 4HO, was produced; even when excess of sulphate of copper was boiled with the precipitated and washed oxide still the subsulphate, SO_3 3CuO, 2HO, was formed; and when in addition to these unsuccessful attempts to obtain it, the modes described being so distinct and easy of execution, we take into consideration that water is not mentioned as a constituent of this disulphate, which is also described as a green-coloured powder,—and no salt of copper whatever is known that possesses a green or a blue colour unless water be present—I am compelled to deny the existence of Thomson's disulphate. Of the non-existence of the octosulphate of Dr. Kane I am not prepared to speak so decidedly; the evidence of the existence of such a salt is so complete and circumstantial, that on a *primâ facie* view of the description and analysis of this salt in the paper "On the Compounds of Ammonia," it almost compels belief. The production of this very singular salt is dependent, according to Dr. Kane's description, upon "the quantity of alkali employed in the precipitation; where potash had been used, there were two distinct precipitates produced, the one the bluish-green generally described, the other 'the octosulphate' of a clear grass-green, resembling that of hy-

drated oxide of nickel. When ammonia was employed the former alone was produced, and the formation of the latter was found to occur where the whole of the copper had been thrown down, but the liquor had not yet begun to react alkaline..... It was found in the first instance accidentally, but I have since seldom failed in preparing it completely pure." The process thus laid down I have followed; and have tortured it in every way, using hot and cold, weak and strong, solutions—adding potash till the solution was perfectly neutral, and also until it became distinctly alkaline, but all to no purpose; I could in no way, nor in a single instance, obtain a salt containing less sulphuric acid than the pentasulphate, SO_3 5CuO, 6HO. When an excess of alkali was added, the precipitate would often change to a greenish-brown tint, but all my efforts to obtain the green salt described by Dr. Kane were fruitless. The composition assigned to this salt, SO_3 8CuO, 12HO, is a most singular and extraordinary one, and on account of this singularity it deserves considerable attention; if a portion of this salt be sent to me I will submit it to analysis, and should it really be found to exist, shall be happy to bear witness to that effect; but at present must confess that I do not believe in its existence. I perhaps may be pardoned the suggestion, but it is not impossible, if the solution of potash was not quite free from carbonic acid, that a mixture of subsulphate, hydrate, and carbonate of copper might be obtained, which on analysis, reckoning the carbonic acid expelled by the second heating with spirit lamp as water, would afford results closely approximating to such a constitution as SO_3 8CuO, 12HO.

On a review of these subsulphates, the question respecting the function of the water contained in them naturally presents itself, and it is one well worthy consideration on account of the highly distinguished authorities who have advocated particular theories on this subject, which at present are usually admitted, or at least are not disputed.

Professor Graham, in the paper "On the Constitution of the Oxalates," &c. &c., seems to decline the question, for speaking of the subsulphates of copper and zinc, he says, "When most successfully prepared they were found to contain four atoms of metallic oxide to one of acid (instead of three atoms of oxide, as M. Berzelius supposed)." Berzelius supposed rightly, there is a trisulphate, "together with four atoms of water. I have not hitherto been able to form a distinct idea of their constitution, or to decide between different views which may be taken of it;" yet in the previous page Mr. Graham writes, "In a former paper upon water as a constituent of sulphates, I examined particularly the constitu-

tion of hydrated sulphuric acid and of the sulphates of the magnesian class of oxides" (copper is included in this class). "All these salts contain one atom of constitutional water;" and again, "all salts are neutral in composition." Now it appears to me that if these two laws be true, that not only should all these subsulphates of copper lose all their combined water save one equivalent, but also, as all salts are neutral salts, that water replaces sulphuric acid with the oxide of copper, thus playing the part of an acid, or *vice versâ*; the first view is not borne out by experiment, and the second exhibits either water or oxide of copper in a new and singular point of view, as possessing both basic and acid characters; in sulphate of water or sulphate of copper, a base; in the subsulphates of copper, either the water or the oxide of copper, an acid. Whether the true meaning has been attached to the laws quoted as laid down by Mr. Graham, I am unable to say. If I have misunderstood his meaning, the misstatement has been unintentional, and is owing to having accepted these sentences for what they express, viz. that all sulphates of the so-called magnesian class of oxides contain an atom of constitutional water, and that all salts are neutral. I presume, however, that the subsulphates of copper will be added to the already somewhat long list of specified exceptions to this latter law. In his 'Elements of Chemistry,' p. 169, Mr. Graham, speaking of subsalts, says, "The compounds of the present class appear to be salts which have assumed a fixed metallic oxide in place of this water," that of crystallization, "they may therefore be truly neutral in composition, the excess of oxide not standing in relation of base to the acid." And this passage surely bears out the meaning I have attached to the former expressions, and is wholly incompatible with the observed facts relative to the subsulphates of copper; for under this view there should be but one, viz. $SO_3\,HO + 5CuO$, corresponding with the crystallized blue sulphate of copper, a compound at present not known to exist.

I now come to Dr. Kane's views on this point. In the paper already referred to, he likewise assumes as a "general principle that the transition from the neutral to the basic condition in salts takes place by the replacement of water by metallic oxide, has, as I conceive, received the fullest confirmation." This is clear and distinct, but I submit that this "general principle" is overthrown by what we have seen to be the constitution of the various subsulphates of copper. Further on it is stated, that "a great number of circumstances conspire to render the derivation of the basic sulphates of the

magnesian class, from the neutral condition, exceedingly complicated. Thus the neutral salts crystallize with quantities of water variable within very extensive limits, and the proportion of metallic oxide by which it may be replaced is subject to variations equally wide: moreover, the replacement of the water by metallic oxide may be but partial, and hence the different hydrated conditions in which the basic salts exist. From these causes may be deduced the possible existence of a very extensive series of basic sulphates varying considerably in type, and *subject only to the one restriction*, that in all their different conditions the sum of the equivalents of water and metallic oxide shall always be equal to the sum of the same constituents in some one of the forms in which the neutral salt may crystallize." To show how far the "one restriction" of this law holds good with the subsulphates of copper, we find that the blue and the green crystallized neutral sulphates of copper contain respectively 1 equivalent base and 5 water =6 equivalents of water and metallic oxide to one of acid, and 1 equivalent of oxide and 1 equivalent of water equal to 2 equivalents to one of acid, whilst the subsulphates contain respectively five, seven, eight, nine, and eleven equivalents of oxide and water together, combined with one of acid; thus in no one instance do the subsulphates of copper agree with the law laid down by Dr. Kane for regulating the constitution of basic sulphates. True it is that Berzelius assigns the composition SO_3 3CuO, 3HO equal to 6 equivalents of water, and metallic oxide to one of acid; but, as has been before stated, I believe one of these equivalents of water to be hygrometric, and that its true constitution is SO_3 3 CuO, 2 HO.

Being thus compelled to differ from those distinguished chemists who have preceded me in these inquiries into the constitution of subsalts and of the subsulphates of copper, I would submit the following idea of the constitution of this class of salts, at the same time distinctly refusing to draw any general conclusion from a rule which I only know is in accordance with observations upon one particular class of salts. I consider the subsulphates of copper to exist as anhydrous sulphate of copper combined with two or more equivalents of hydrated oxide of copper; these compounds, in most instances, unite with definite proportions of water, precisely in the same manner as some neutral and acid salts combine with water of crystallization, which like them they part with at stated elevations of temperature.

This view is completely borne out by the subjoined tabular arrangement of all the subsulphates of copper I have been able to procure. Could I consent to consider either

the water or the oxide of copper as standing in the same relation to the other as an acid does to its base, Mr. Graham's theory of the constant neutrality of salts, as applying in this instance, might readily be admitted; but believing both of them to be only capable of acting as basic oxides, I am compelled to reject it, and admit the existence of basic as I do of acid salts.

Sulphates of Copper.

Anhydrous neutral sulphate.	$SO_3\,CuO$.
Green neutral sulphate .	$SO_3\,CuO + HO$. (Thomson.)
Blue neutral sulphate .	$SO_3\,CuO + 5\,HO$.
Trisulphate	$SO_3\,CuO + 2\,CuO\,2\,HO$.
1st tetrasulphate . . .	$SO_3\,CuO + 3\,CuO\,3\,HO$.
2nd tetrasulphate . . .	$SO_3\,CuO + 3\,CuO\,3\,HO + HO$.
3rd tetrasulphate . . .	$SO_3\,CuO + 3\,CuO\,3\,HO + 2\,HO$.
1st pentasulphate . . .	$SO_3\,CuO + 4\,CuO\,4\,HO$.
2nd pentasulphate . . .	$SO_3\,CuO + 4\,CuO\,4\,HO + 2\,HO$.

XXXVII. *On the Spontaneous Change of Fats.* *By* W. Beetz, *Esq.*

Read April 18, 1843.

WE sometimes find in various parts of mines, which have not been worked for a considerable time, fragments of a white brittle substance having frequently the appearance of fat, but at times so changed that it presents more the aspect of a mineral body; I am not aware that any one has examined this substance, and was consequently very much pleased at receiving some pieces of it from different mines.

The first specimen was very brittle, so that it could be rubbed to a fine powder; its appearance was that of tallow. The exterior was a little covered by sesquioxide of iron, but the interior was quite clean. It was found in the "Old Man" iron mine, Xiffau near Runderroth, in the district of Oberberg. It was dissolved by boiling alcohol without residue, but on cooling was deposited as a flocculent precipitate. Warm æther dissolved it very easily, and from this solution it could be crystallized. When boiled with an alkali, it was converted perfectly, but not very easily, into soap. Submitted to destructive distillation the products were the same as those of all fats containing glycerine, as was fully evidenced by the intense and peculiar smell.

It melted at 59° C. into a perfectly clear liquid.

The analyses of this body showed its composition to be as follows:—

I. 0·323 gr. of the substance gave 0·349 gr. of water and 0·904 gr. of carbonic acid.

II. 0·314 gr. gave 0·352 gr. of water and 0·878 gr. of carbonic acid.

III. 0·316 gr. gave 0·361 gr. of water and 0·878 gr. of carbonic acid.

These results, calculated to the hundred parts, give the following results:—

	I.	II.	III.
Carbon . .	76·32	76·25	75·78
Hydrogen .	12·00	12·45	12·69
Oxygen . .	11·68	11·30	11·53
	100·00	100·00	100·00

This composition is the same as that of stearine from mutton tallow, according to the authority of Lecanu. I insert here an analysis of stearine, made by Liebig and Pelouze, and the result of their calculation, in order to compare them with the analysis made by myself.

Liebig and Pelouze.	Calculated.
146 C = 76·14	76·21
236 H = 12·30	12·18
17 O = 11·56	11·61
100·00	100·00

The solubility of the substance is also the same as that of stearine, and the difference of the temperatures at which the two bodies melt is very small. The melting point of stearine is 62°, that of the body under examination 59°, while that of tallow is not more than 37° C.

A portion of the body was saponified by soda. The soap was solid and hard, and when dissolved in hot water it formed on cooling a gelatinous mass, even when the quantity of soap was very small. It was decomposed by hydrochloric acid, and the fat acid obtained in this manner was also hard and brittle; its melting point was 60° C.

On burning the acid with oxide of copper, the following result was obtained:—

0·3215 gr. of the substance gave 0·3715 gr. of water and 0·836 gr. of carbonic acid.

This composition, calculated to the 100 parts and compared with the analysis and the calculation of stearic acid made by Berzelius, gives the following results:—

	Calculated.	Berzelius.	Found.
70 Carbon	= 79·963	80·145	79·40
134 Hydrogen	= 12·574	12·478	12·81
5 Oxygen	= 7·463	7·377	7·79

It cannot be supposed that this fat came into the mine in the form of stearine, but most probably it had been a miner's candle, and had probably been changed into stearine by the continuous action of water, for the composition of stearine differs from that of tallow in its containing a greater per-centage of carbon. Tallow contains to 100 parts of carbon, 14·81 hydrogen and 11·76 oxygen. Stearine to the same quantity of carbon, 16·02 hydrogen and 15·14 oxygen; so that this change can be accounted for by supposing that the tallow had combined with water, at the same time that it lost carbonic acid. The conditions necessary to this process are always found in mines, water is present, and the admittance of air is not required.

Another piece of fat was found in the mine Frederic near Tarnowitz; its appearance was the same as that of the first substance. By boiling alcohol and æther it was not perfectly dissolved. The substance was carefully cleaned outside, and then the exterior portions as well as the interior examined. From the exterior 0·317 gr. were finely scraped and boiled with alcohol, then filtered and washed. The filtered solution was precipitated by water, and weighed 0·057 gr. The residue was boiled with hydrochloric acid; the weight of the fatty body that was hereby separated was 0·232 gr. The liquid contained nothing but lime in solution, which determined as carbonate weighed 0·044 gr., and is equivalent to 0·025 gr. of caustic lime. The melting point of the fat, soluble in alcohol, was 58° C., that of the fat acid, separated by hydrochloric acid, 60° C. The first fat was from all its reactions stearine, the second stearic acid, so that the substance was composed of 0·257 gr. stearate of lime and 0·057 gr. stearine, or in 100 parts of 17·98 stearine, 7·88 lime, and 73·18 stearic acid. The proportion of lime and stearic acid in the soap is the same as that in the soap prepared in the common manner; for if we calculate the composition of the 81·06 grs. lime-soap, which the substance contains, we obtain the following values:—

	Found.	Calculated.
Stearic acid . .	73·18	73·20
Lime	7·88	7·86
Stearine . . .	17·98	
	99·04	

This composition is confirmed by a second combustion of another portion of the same body.

0·317 gr. of the substance gave 0·833 gr. of carbonic acid and 0·338 gr. of water. If we calculate these numbers to their equivalents in 100 parts, and if the substance consists indeed of

stearine and stearate of lime, the resulting values must be the same as those which can be calculated from the known composition of stearine and stearic acid. This is the case in the following table.

	Stearic acid.	Stearine.	Calculated.	Found.
Carbon .	58·54	13·70	72·24	71·66
Hydrogen	9·22	2·19	11·41	11·84
Oxygen .	5·42	2·09	7·51	8·62
CaO . .	...	...	7·88	7·88
	73·18	17·96	99·04	100·00

0·986 gr. of the inner portion of the substance was boiled with æther, the solution evaporated and the fatty matter fused, it weighed 0·709 gr.; the residue, 0·277 gr., was decomposed by hydrochloric acid; it gave 0·249 gr. of a fat acid and 0·047 gr. of carbonate of lime, equivalent to 0·026 gr. of lime. If we calculate these values to the 100 parts and compare them with the numbers derived from the known composition of stearate of lime, and deduct the ascertained amount of the stearate, the remainder will represent the stearine.

	Found.		Calculated.
Lime	2·64	28·09	2·70
Stearic acid . .	25·25		25·39
Stearine . . .	71·90		71·91
	99·79		100·00

In the inner part, consequently, the substance consisted more of stearine and less of soap than on the exterior parts, so that the saponification, which began through the medium of the adjacent lime, is not yet complete, but is more advanced in the exterior portions than the interior.

This substance probably had the same origin as the first specimen; it is very similar to adipocire discovered by Fourcroy, and which Chevreul has proved to be human fat partly saponified, the bases of which are ammonia, from the nitrogenous compounds of the human body, and magnesia and lime, from the bones. The process of saponification took place in this, as well as in the described substances, by the long continued action of the materials on each other, which action is not as yet perfected. The change of fats into stearine has many analogies in the manufacture of candles. The manufacturer of stearine candles prefers using tallow of from one to two years old, because it yields a larger profit, and the fat looks a little whiter than fresh tallow. If a piece of mutton tallow is broken asunder and lies in a warm room, the fracture-surface is soon covered with an oily substance, the elaine, which is present in great abundance. The surface of an old fat, treated

in the same manner, remains dry and without this oily aspect, because it does not contain so much elaine. The fact that tallow candles become whiter after some time, is not of this nature, because it demands the presence of air, and the candles do not become hard, but tough.

Another occurrence that gave rise to a product quite resembling the described fats must here be mentioned. In a manufactory of candles in Berlin the tallow was poured into a large box; the door of this, by which the fat was taken out, was one day not well closed, some of the fat consequently ran out, and remained under the box during ten years. After this time the box was taken away, and the fat was now found quite hard and brittle. I have not been able as yet to obtain any of this substance in order to examine the changes it had undergone. In a fat of a few years old it would be always difficult to show the change into stearine by an analysis of the elements, for the change could not as yet be very advanced, and the composition of the fat would not therefore be very different from that of stearine. The conditions necessary to the above mentioned change are the same in the mine as in the cellar where the box stood; in both water was present, but not a free passage of air. The change in the two first cases had been going on for a long time, for it can be shown that the fat had been in the mines during more than a hundred years. If this one condition could be supplied by another, so that the fat could be changed readily by an artificial process into stearine, it would not be necessary to consider the elaine as a disagreeable addition and to connect it to a bad and cheap product, but the whole substance could be worked as stearine, or from the whole quantity stearic acid could be obtained.

The substances described prove the truth of the supposition which Liebig has made in his last treatise "On the production of Fat," that liquid fats can be changed into hard ones.

XXXVIII. *On certain Improvements in the Instrument, invented by the late* Dr. Wollaston, *for ascertaining the Refracting Indices of Bodies. By* John Thomas Cooper, *Esq.*

Read April 18, 1843.

THE ordinary physical characters of substances such as hardness, colour, lustre, fracture, specific gravity and some others, have been the means which chemists and mineral-

ogists have long been in the habit of employing for the identification both of inorganic and organic substances; and I think it will be acknowledged by all who give their attention to such matters, that any additional means added to the above modes of observation, if it be capable of being put into practice with equal facility, and with a certainty of giving results with a degree of precision little, if at all inferior to that which is capable of being attained by the balance, is a sufficient apology for occupying a short time of the Chemical Society.

About forty years ago, the late Dr. Wollaston described in the Philosophical Transactions, an ingenious instrument by which the refractive indices of substances, either in a solid or liquid state, could be with facility determined, the method requiring extremely small quantities of the matter to be subjected to experiment, was an additional recommendation for its adoption in practice, but it has never been generally brought into use; and the cause which in my opinion has operated more than any other to prevent its more extended employment in the laboratory of the chemist, is the limited extent of substances which, in the form he gave it to the world, could by its means have their indices of refraction determined with accuracy. It is with the view of rendering the method of Dr. Wollaston more generally known, and of putting the Society into possession of a knowledge of some alteration in the construction of the instrument, by which it is rendered of a more extended application, that I have ventured to call the attention of the Society to this subject.

Instead of employing only one species of glass as recommended by Dr. Wollaston, I make use of several, each of which is suited to the nature of the substance under examination, and that species of glass is selected for the purpose, which, when the substance to be examined is applied to the base of the prism, gives with the subject so applied, when viewed in its position, neither too acute or too obtuse an incidence; for it is at extreme incidences, as far as I have been able to observe by the means here employed, that erroneous results are liable to be obtained. The glass prisms which I am in the habit of using have respectively a refractive index for Fraunhofer's ray *b* of

1·516, which is ordinary plate glass.

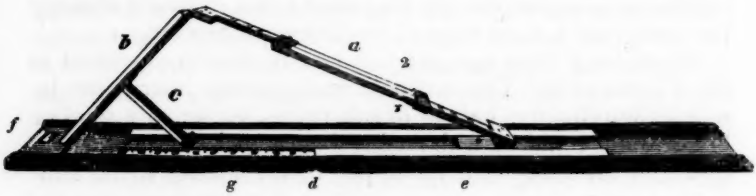
1·583, which is common flint glass.

1·635, a very heavy flint glass, which I made some years ago for optical purposes.

1·816, Faraday's borate of lead glass.

Now in order that these different prisms may be used, a modification of the apparatus as originally proposed by Dr.

Wollaston is requisite, or otherwise each prism will require a separate and distinct instrument; but to accomplish this object with but one instrument, I have changed the position of the indicator from the longer of the bars to the shorter, and constructed the longest bar *a* in such a manner that it is capable of being extended in length from 15·16 to 18·16 inches,



while the height of the shorter bar *b* retains the original length proposed by Dr. Wollaston of ten inches, and the indicator *c*, as a consequence, has only the half of this length, that is to say five inches. The bottom bar *d* is about two feet in length, and has a dovetailed groove or furrow ploughed in it throughout its whole length; in this groove a piece *e* is made to slide easily, which may be clamped or made fast by means of a thumb-screw in any part that may be required. To this sliding piece is attached a hinge, and to this hinge is also attached one of the sliding bars 1, the other sliding bar 2 being hinged to the bar *b*. These sliding bars are capable of being fixed at any required length, by means of a clamping-screw. The bar *b* is hinged to an immoveable block *f* of about two inches square, having an excavation of about three quarters of an inch square formed in it, for the purpose of preventing the substances submitted to experiment, on being placed on the base of any one of the prisms, from coming into contact with the wood of which the block is made. Exactly in the middle of the bar *b* is hinged the indicator *c*, which is of brass and is filed to a very sharp edge; it is precisely five inches in length from the centre of the hinge to its extremity. This indicator may be slid along the graduated scale *g* which is laid down on the upper surface of the bottom bar *d*, and by means of the pressure of the short bar *b* to which it is attached, will remain in close contact with the graduated scale in whatever position the bars are capable of being placed; the sharp edge of the indicator is always perpendicular (provided the lengths have been duly attended to, by which is meant the precise distances of the centres of motion of the hinges from each other) to the axis of the hinge which connects the bar *b* with the moveable bar *a*.

It now only remains to be stated in what manner the instrument is to be adjusted, which is to be effected in the following manner:—When a piece of glass has been selected that is capable of giving with the substance under examination a total reflexion at a mean incidence (by which is meant, when the total reflexion occurs at an angle varying from about 35° to 65°), supposing this to be the case with a prism whose refractive power is 1·635, such as would be required to obtain the refractive power of any or most of the fixed oils, then the adjustable bar is to be made sixteen inches and thirty-five hundredths of an inch in length between the centres of the pins of the hinges, and the bottom bar to be shifted until the brass edge of the indicator stands at ·635 on the scale; the substance on being applied to the base of the prism is then to be put into its situation on the block, and the whole apparatus placed in such a way that the light from the sky may fall and be reflected from the base of the prism.

The eye being directed along the upper edge of the short or ten-inch bar, the latter is to be elevated or depressed just until the faintest gleam of the substance is to be seen in the bright light reflected from the prism's base, and which, if properly managed, will appear of a very pale blue or bluish-green colour; when this occurs the indicator will point out the refractive power of the substance under examination. If a very volatile substance, such as any of the æthers or hydrocyanic acid, should be the subject of experiment, I then am in the habit of employing a small piece of flat glass of a dark colour attached by means of the fluid, to be examined, with a very slight pressure to the base of the prism; this will effectually prevent evaporation of the fluid for a period of sufficient duration to enable any one with ease and precision to determine the refractive index or power of such a substance; and in general I prefer using this for all liquids, as it permits a more extended and uniform surface of the matter under examination, and diminishes the liability to error.

XXXIX. *On Theine and its Preparation.*

By John Stenhouse, *Esq.*, *Ph.D.*

Read May 2, 1843.

[Continued from page 221.]

Complete Analysis of the Theine prepared by Sublimation.

0·285 gr. of the substance gave 0·5125 carbonic acid and 0·132 water. When burnt with oxide of copper, eight tubes gave carbonic acid and nitrogen in the proportion of four to one.

	Found.	At.	Calculated numbers.
Carbon	49·72	16 Carbon	=49·798
Hydrogen	5·14	10 Hydrogen	= 5·082
Nitrogen	28·78	2 Nitrogen	=28·832
Oxygen	16·36	4 Oxygen	=16·288
	100·00		100·000

Theine from Paraguay Tea.

Through the kindness of my friend Professor Gardner, I have procured an additional quantity of Paraguay tea, which has enabled me to complete the analysis of the theine it contains, and also to determine its quantity. The easiest and most œconomical way of obtaining theine from Paraguay tea is by sublimation. The filtered infusion of the tea, after being treated with acetate of lead and the precipitate removed, should be boiled with an excess of litharge, the clear liquid evaporated to dryness and sublimed with the usual precautions. One quantity of two pounds yielded 12·5 grs. of anhydrous theine, and a second quantity of equal amount, which was more successfully treated, gave 14·5 grs. = 0·13 per cent. This is about half the quantity which most kinds of coffee yield, which I have found to vary from 12 to 18 grs. for a pound, and about ten times less than Chinese tea, a pound of which yields from 70 to 90 grs.

Analysis of Theine from Paraguay Tea.

I. 0·2095 gr. of the substance dried at 212° gave 0·525 carbonic acid and 0·134 water.

II. 0·3192 gr. gave 0·572 carbonic acid and 0·1487 water.

When burnt with oxide of copper, nine tubes gave carbonic acid and nitrogen in the proportion of four to one.

	Found. I.	II.	At.	Calculated numbers.
Carbon	49·960	49·54	16 Carbon	=49·798
Hydrogen	5·145	5·17	10 Hydrogen	= 5·082
Nitrogen	28·927	28·68	2 Nitrogen	=28·832
Oxygen	15·968	16·61	4 Oxygen	=16·288
	100·000	100·00		100·000

The following is a more complete analysis of the double salt of muriate of theine and chloride of platinum:—

I. 0·4637 salt gave 0·412 carbonic acid and 0·1155 water.

II. 0·4347 gave 0·386 carbonic acid and 0·1184 water.

I. 0·461 salt gave 0·112 plat. = 24·29 per cent.

II. 0·529 salt gave 0·130 plat. = 24·57.

III. 0·5828 salt gave 0·143 plat. = 24·53.

IV. 0·458 salt gave 0·112 plat. = 24·45.

I.	II.	At.	Calculated numbers	per cent.
C 24·56	24·55	16 C =	1222·9	24·32
H 2·76	3·02	11 H =	137·2	2·72
		4 N =	708·1	14·08
		4 O =	400·0	7·96
		3 Cl =	1327·9	26·41
Pt 24·46	24·46	Pt	1233·2	24·51
			5029·3	100·00

The rational formula for the salt is $C_{16}\ H_{11}\ N_4\ O_4\ Cl\ H + Pt\ 2\ Cl$. The formula for Theine,—

16 Carbon	= 1222·96
11 Hydrogen	= 124·79
4 Nitrogen	= 708·16
4 Oxygen	= 400·00
Atomic weight	= 2455·91

Nitro-theine.

I have given the provisional name of nitro-theine to the substance crystallizing in large shining plates, produced by the long-continued action of an excess of boiling nitric acid upon theine. It is not necessary to employ fuming nitric acid to obtain this substance, acid of the ordinary strength answers equally well. Nitro-theine when crystallized out of water forms large shining plates resembling cetine, but having more of a pearly lustre. When sublimed, its crystals resemble those of naphthaline, and when formed by spontaneous evaporation from æther they are deposited in large, very regular rhombohedrons. I formerly stated that alkalies do not evolve ammonia from nitro-theine; I find that in this I was mistaken, for when boiled with solution of potash it gives off abundance of ammonia.

When subjected to analysis,—

I. 0·2628 gr. of the substance dried at 212° gave 0·398 carbonic acid and 0·1005 of the water.

II. 0·2529 gr. gave 0·3855 carbonic acid and 0·0975 water.

When burnt with oxide of copper, ten tubes gave carbonic acid and nitrogen in the proportion of five to one.

	I.	II.
Carbon	41·87	42·15
Hydrogen	4·24	4·28
Nitrogen	19·39	19·56
Oxygen	34·50	34·01
	100·00	100·00

Nitro-theine appears to be a neutral body, and as I have not been able to determine its atomic weight, I have not

thought it worth while to attempt to deduce any formula from these analyses. Theine does not yield more of this substance than from 5 to 6 per cent.

XL. *On the Composition of an Acid Oxide of Iron (Ferric Acid).* *By* J. Denham Smith, *Esq.*

Read May 16, 1843.

IN the autumn of the year before last, whilst pursuing some investigations respecting the alleged conversion of carbon into silicon, I remarked that when the residuum of the calcination in close vessels of ferrocyanide of potassium (carburet of iron) was fused with carbonate and nitrate of potash, and the resulting compound treated with water, a solution of a deep amethystine red colour was produced; this rapidly decomposed, evolving oxygen gas, and depositing sesquioxide of iron, until the decomposition being completely effected, it became quite colourless; no manganese could be detected in the solution, nor in the deposit, although the colour of the former was precisely similar to the permanganate of potash in solution.

Remembering that the combination of an oxide of iron with potash was already on record, but unable to recall to memory the publication in which it was noticed, I am indebted to the Editors of the Philosophical Magazine for referring me to the *Journal de Pharmacie*, tom. xxvii. p. 97, where I found a communication from M. C. le Fremy, upon "The Action of the Alkaline Peroxides on Metallic Oxides." Since the appearance of this memoir, which has been followed by researches by the same author on the combination of potash with the oxides of zinc, tin, &c., various notices have been published by MM. Trommsdorff, Wackenroder and Poggendorff, on the subject of this combination of oxygen, potassium and iron, confirming the existence of this purple-red compound, and pointing out various modes of obtaining it.

I had expected that M. Fremy would have extended his inquiries and ascertained the composition of this new oxide of iron; but as a considerable period has elapsed since his original notice of its existence, and his subsequent researches in connexion with this subject having taken other directions, other chemists also having investigated the compound, and as my own experiments were commenced before I was referred to M. Fremy's paper, I may be excused for having thus directed my attention to the composition of a substance, to the priority of the discovery of which I have no claim, although I had ascertained its existence independently of the observations

of the French chemist. I have entered on this explanation, as I would in nowise wish to deprive M. Fremy of his just claim to the original notice of this compound; but as my previous observations and pursuit of the subject were entirely independent of M. Fremy's notice of its existence, I feel myself justified in communicating the results of my investigations, especially as its first discoverer appears to have abandoned the pursuit.

In the memoir in the *Journ. de Pharm.* already alluded to, various modes are pointed out for preparing this combination of potash and oxide of iron, which is obtained by igniting a mixture of sesquioxide of iron, potash and nitre, or peroxide of potassium and sesquioxide of iron, or by calcining at a full red heat potash and sesquioxide of iron; by these means a brown substance was procured which afforded a deep violet-red coloured solution, very soluble in water, but which solution is easily decomposed; concentrated solutions of the alkalies precipitate it of a brown colour, which precipitate redissolves on the addition of water; it decomposes rapidly by an elevation of temperature, and instantaneously by the contact of organic substances. The same coloured solution may be formed by passing a current of chlorine through a concentrated solution of potash, holding precipitated sesquioxide of iron in suspension. The German chemists prefer deflagrating dry nitrate of potash with half its weight of iron-filings at a temperature approaching to visible redness, and also direct the employment of chlorine gas, potash and precipitated oxide of iron, as mentioned by M. Fremy, to procure it. M. Poggendorff found that when a current from Grove's battery is passed through a solution of one part of hydrate of potash in four of water, using *cast iron* for the positive pole plunged in the potash, and wrought iron or any other convenient metal as the negative pole, ferrate of potash was formed in the solution, which immediately becomes dark red and opake. Wrought iron and steel do not produce this compound, but evolve oxygen gas; the red solution soon decomposes either with or without the continuance of the passage of the electrical current, oxygen gas being liberated and sesquioxide of iron precipitated.

To prepare this compound I have found the subjoined process attended with very uniform success:—Wash the ferri sesquioxydum of the shops with boiling water until free from sulphate of soda, dry and ignite at a low red heat; this furnishes a very pure oxide of iron and in a state of minute division; one part of this is to be intimately mixed with four of dried nitre, reduced to fine powder; place this mixture

in a crucible of about twice the capacity of the bulk of the mixture, lute a well-fitting cover on, making a few small holes in the lute to allow the escape of gas, and ignite at a *full red* heat for about an hour, if six or eight ounces are made: the time of ignition depends much on the quantity prepared, and the temperature should never be raised above a full red. When well prepared it presents the appearance of a dark reddish-brown porous mass, rapidly deliquescing on exposure to the air, so that I have found it advantageous to powder it whilst still warm, when it may be preserved for use in a well-stoppered bottle, apparently for any length of time.

To examine the solution of this substance it is most convenient to employ ice-cold water, as much heat is evolved when it is thrown into water, and the decomposition of the solution is augmented or retarded by the elevation or depression of temperature. On the addition of water it evolves much oxygen gas with effervescence, probably owing to the decomposition of peroxide of potassium; if the water employed be ice-cold and the vessel containing it plunged in ice, the decomposition of the solution will be retarded. By allowing the mixture to subside for a few minutes, a solution is obtained almost free from oxide of iron in suspension, of so deep an amethystine red colour as to be apparently opake except at the edges, but by dilution its colour is readily perceived; it gradually decomposes, evolving oxygen gas and depositing sesquioxide of iron; heat facilitates this decomposition; at 212° F. it is completely effected, and the solution remains colourless. It is decomposed, evolving oxygen, by sulphuric and nitric acids, chlorine is liberated by the addition of hydrochloric acid; by oxalic acid, carbonic acid gas mixed with oxygen is given off. It affords no precipitate with the salts of lime, magnesia, or strontian, but on the addition of a barytic salt a voluminous crimson-red precipitate falls, which may be washed, collected and dried at 212° without changing colour. With the metallic salts, the bases of which are capable of combining with more than one equivalent of oxygen, as nickel, manganese, &c., it produces the superoxide of these metals, but with the salts of zinc and metals combining with but one equivalent of oxygen, it precipitates their oxides and evolves oxygen gas.

When the deep pink-coloured solution is prepared by passing a current of chlorine gas through concentrated solution of potash holding oxide of iron in suspension, or through the deep amethystine solution already described, keeping the vessel cool during the passage of the gas, the solution obtained

is of a lighter colour than the amethystine liquid and very permanent, it having been kept for months in close vessels without decomposition being completely effected, the gradual progress of which however is shown by the deposition of a light brown substance (sesquioxide of iron?). This chlorinated solution may even be evaporated and a pink salt obtained, but I have been unable to isolate by any means I have attempted the potash salt of this oxide of iron. I may add, that the characters assigned to these two solutions by the French and German chemists are generally in accordance with my own observations.

Although foiled in my endeavours to obtain the potash salt free from admixture of other salts, I was yet enabled to deduce from it the composition of this new oxide of iron, which in accordance with my suggestion, Sept. 1841, is now usually called ferric acid, and subsequently to confirm this constitution by the analysis of the barytic salt.

The mode of analysis was extremely simple, being founded on the perfect decomposition of the deep amethystine solution at 212°. A solution of the reddish-brown fused mass was prepared with ice-cold water and with the precautions before described; when the insoluble portion had subsided, which it did rapidly, and a portion of the solution had been tested by withdrawing it by a tube and mixing with a large quantity of distilled or of lime water (which latter seems to possess the property of checking the rapidity of the decomposition of this potash salt when very dilute), to ascertain whether the subsidence of the uncombined oxide of iron was so complete that an apparently inappreciable quantity was held in suspension; a certain quantity of this clear amethystine solution was transferred to a retort of a known capacity—leaving, of course, a portion of atmospheric air in the upper part of the body and in the neck of the retort; this quantity of air was accurately determined by previous measurements and graduation of the retort; heat was then applied, and the contents of the retort raised to violent ebullition which was continued so long as any gas was evolved; these gaseous products were collected over water, and when no more gas was liberated absorption was allowed to take place by withdrawing the lamp from the retort; any air which the retort then contained was added to that already collected, and when the gas had acquired the temperature of the surrounding atmosphere, it was measured, the known bulk of atmospheric air originally contained in the neck and upper part of the retort subtracted from it, and the residue, oxygen, corrected for temperature and pressure.

The oxide of iron deposited during the boiling was dissolved in hydrochloric acid and estimated in the usual way.

I subjoin the detail of an analysis as an example*. The results of several successive experiments are contained in the following table:—

Exp.	Cub. in. at 60° and 30.	Grs. of oxygen.	Grs. ox. iron.	Total wt. of oxygen.	Weight of iron.
1	12·3	4·2	16·4	9·12	11·48
2	9·38	3·37	12·6	7·15	8·82
3	13·03	4·45	16·8	9·49	11·76
4	5·21	1·78	7·2	3·94	5·04
5	14·70	5·03	22·3	11·72	15·61
6	7·58	2·59	10·6	5·77	7·42
7	33·41	11·41	42·0	24·01	29·40
	96·11	32·83	127·9	71·20	89·53

The mean of these experiments gives 22·27 parts of oxygen by weights to 28 parts or one equivalent of iron, which is equal to a deficiency of 1·74 parts in three equivalents, or 24 parts of oxygen. This is, I submit, an approximation sufficiently near to three equivalents of oxygen to one of iron, to justify me in adopting the formula FeO^3, as representing the constitution of this acid oxide of iron; especially when we consider that the circumstances under which the experiments were made would indicate the probability of some free sesquioxide of iron being suspended in the solution, as, from the unstable nature of the compound, a short period of time only could be allowed for the deposition of any insoluble matter, and the impossibility of subjecting it to filtration, owing to its decomposition by the contact of organic substances. This excess of oxide of iron varies in the different experiments quoted, so that whilst Nos. 4, 5, and 6 afford 21 to 22 parts oxygen to an equivalent of iron, 1, 2, 3, and 7 all exceed 22 of the gas to an equivalent of the metal, the last, No. 7, especially; and this experiment being the one upon which I am inclined to place the greatest reliance from the concentrated and clear state of the solution, gives nearly 23 parts (22·85) of oxygen to 28 iron. This cause, together with a certain amount of decomposition during the transference from the vessel in which the solution was made to the retort, affords an explanation of the deficiency in the quantity of oxygen as indicated in every experiment, in comparison with that which I theoretically assign to this compound.

* A retort filled to a certain limit with the solution left 13·75 cub. in. of atmospheric air in the body and neck of the retort, and gave 26 cub. in. of gas at a temperature of 58°, and barometer at 29·9 26 − 13·75 air = 12·25 oxygen corrected, weighs 4·2 grs. The oxide of iron freed from silica by hydrochloric acid and ammonia, gave 16·4 grs. of sesquioxide = 11·48 iron, and 4·92 oxygen + 4·2 = 9·12 oxygen combined with 11·48 iron.

In no one case was the quantity of oxygen actually obtained so small as to indicate a compound of 20 parts of oxygen to 28 of iron (2 Fe + 5O or $F^2 + O^2$), and I do not consider the formula intermediate with this last and the constitution I have assigned to the oxide, is a very probable one to exist, being 3 F + 8 O; moreover, in four out of seven experiments more oxygen was obtained than such a compound could evolve.

The conclusion at which I arrived, that this ferric acid is a *teroxide of iron*, is confirmed by the subsequent examination of the insoluble crimson compound it forms with barytes. This salt is readily formed by adding an excess of a dilute solution of a barytic salt to the clear amethystine solution, which, prepared as I have described and dissolved in close vessels, will not contain the sulphates in any marked quantity, nor any carbonic acid whatever, the precipitate being washed in vessels excluded from the atmosphere with freshly boiled distilled water, to prevent the access of carbonic acid to the alkaline solution, and drying at 212° F. It is of a dark crimson red colour, decomposable before drying by the mineral acids, including carbonic acid, but less readily by sulphuric acid than by the others. When strongly heated it evolves water and oxygen gas. As diluted nitric acid appeared to decompose this salt without the formation and evolution of any but oxygen gas, I selected this acid as the agent of analysis.

Having procured a very thin light flask with a long narrow neck of the capacity of about four fluid ounces, it was about half filled with dilute nitric acid, which, together with the flask, weighed 1862·05 grs., to this 33·16 grs. of the red barytic salt were gradually added, a rapid evolution of oxygen ensued with every addition of the barytic ferrate; at the expiration of twenty-four hours the flask and contents were weighed = 1891·94 grs., which indicates a loss of 3·27 grs. of oxygen gas; the solution was of a light pink colour, showing that decomposition was not wholly effected; but this entirely disappeared, and the solution became colourless on the addition of two drops of weak hydrochloric acid to the warm solution, evidencing so small an amount of the undecomposed salt as not to be worth considering: this solution evaporated to dryness, redissolved, and filtered, gave 2·78 grs. of silica and sulphate of barytes. On the addition of sulphate of soda to the solution sulphate of barytes was precipitated, which, washed, dried and ignited, weighed, exclusive of ash of filter, 24·64 grs.; the oxide of iron precipitated by ammonia gave 8·88 grs., leaving 2·09 for water and loss.

A second experiment upon a portion of this salt, prepared

at a subsequent period to that used in the first experiment, and adapting a tube containing chloride of calcium to the flask, gave from 47·47 grs. of the compound, 4·31 grs. of oxygen, and, exclusive of ash of filters, 0·48 grs. of silica, &c., 37·82 grs. sulphate of barytes, and 15·27 grs. of sesquioxide of iron, leaving 2·63 grs. for water and loss.

A third experiment gave 3·06 grs. oxygen, ·69 grs. of silica, &c., 27·163 grs. sulphate of barytes, and 10·86 of oxide of iron from 34·47 grs. of the red barytic salt.

To obtain the water, I merely heated the ferrate gradually and gently on a sand heat till it assumed a greenish colour, rejecting those experiments which were partially converted into a light drab colour, which is an evidence of loss of oxygen. 64·48 grs. of ferrate lost 4·93 grs., and 44·41 lost 2·91 grs.; by ignition this green residue was converted into a drab-coloured powder, apparently with the loss of half an equivalent of oxygen, which residue, treated with dilute nitric acid, evolved oxygen gas. Now, estimating the loss sustained in these experiments as water and taking the mean, ferrate of barytes when pure will contain 7·2 per cent. of water, and the three analyses of this barytic salt should respectively indicate, if the loss sustained in these be only water, 2·18 grs. 3·38 grs., and 2·44 grs., a result, as will be seen by reference, so near the loss sustained in analysis, that the difference may fairly be reckoned as merely an error of experiment. The results obtained from the three foregoing analyses, reckoning the loss as water and deducting the silica and sulphate of barytes as impurities, will give respectively 30·38 grs., 46·99 grs., and 33·78 grs., as the quantities of pure ferrate of barytes operated upon, yielding—

	I.	II.	III.
Barytes	16·14	24·78	17·75
Sesquioxide iron .	8·88	15·27	10·77
Oxygen . . .	3·27	4·31	3·06
Water and loss .	2·09	2·63	2·20
	30·38	46·99	33·78

The mean of which will give 19·56 of barytes, 11·64 of sesquioxide of iron, 3·35 of oxygen, and 2·31 of water contained in 37·06 of ferrate barytes.

The 11·64 parts of sesquioxide of iron are composed of 8·15 of iron and 3·49 of oxygen, which uniting with the 3·55 of oxygen gas (within ·06 of a grain in 37·06 grs. of the quantity theoretically required), will yield 15·19 of teroxide of iron, or ferric acid, combined with 19·56 parts of barytes, indicating the formula $BaO\,FO_3\,HO$ as the composition of this salt.

	Exp.	Theory.
1 equiv. barytes . .	19·56	20·60
1 equiv. ferric acid .	15·19	14·06
1 equiv. water . .	2·31	2·4
	37·06	37·06

I therefore consider the acid oxide of iron present in the deep amethystine solution of the potash salt, and in combination with barytes in the crimson-red barytic salt, to be a teroxide of iron, containing twice the quantity of oxygen existing in the sesquioxide. Whether the pink salt obtained by the agency of chlorine is another and distinct combination of iron with oxygen, forming a still more highly oxygenated compound than ferric acid, I am at present unable to state, but I am inclined to this opinion; it is certain, however, that another acid oxide of iron exists, probably of a lower degree of oxidation than the ferric acid. The combination of this acid with potash or soda is of a beautiful emerald-green colour, precisely similar to the green manganate of potash. The conditions requisite to procure this compound I am at present unable to point out, but I have generally succeeded when I have employed one-half the quantity of nitrate of potash, or what I am inclined to think superior, nitrate of soda, employed to prepare the amethystine salt, and exposed the mixture to a somewhat higher temperature. I have never obtained it unmixed with the purple salt, but owing to its being a much more stable compound than that is, it remains for a considerable length of time undecomposed at ordinary and even elevated temperatures, if excluded from the air. This furnishes an easy method to prove the green salt free from the amethystine salt. Its properties appear analogous to those of the amethystine salts, except with respect to its permanency; acids liberate oxygen, changing the solution to pink, which gradually disappears; chlorine rapidly converts it into the pink salt. It is capable of filtration without being entirely decomposed, but long contact with organic matters appears to resolve it into oxygen and sesquioxide of iron. I regret that at present I have not been able to obtain this green acid of iron in such a state of combination that I can accurately determine its position, but I hope during the next session of the Chemical Society to lay before its members a more detailed investigation of the pink chlorinated compound, and also of the green oxide, and to ascertain their composition and properties.

Romford.

XLI. *On the Action of Alkalies on Wax.* *By* Robert Warington *and* W. Francis, *Esqrs.*

Read May 16, 1843.

FEW subjects have of late engaged so much the attention of chemists as that relative to the formation of fat in the animal organization, a subject fraught with results of the highest importance both to science and its applications to rural œconomy.

Two theories have been proposed to account for its origin:—The one by M. Liebig, which supposes that the fat is produced by the conversion of sugar, starch and other non-nitrogenous bodies during the process of digestion, as detailed in his paper on this subject published in the Society's Memoirs, vol. i. p. 164; a view which is supported by various analogous processes and decompositions with which chemists are already familiar, as for instance the conversion of amygdaline into the oil of bitter almonds, of salicine into oil of meadow-sweet, and also the production of ænanthic æther in the fermentation of amylaceous substances, which moreover has recently been shown by M. Wöhler to be readily converted by distillation into margaric acid. The other theory by MM. Dumas, Boussingault and Payen*, according to which no production of fat takes place in the animal frame, but that it is contained already formed in the various products of the vegetable kingdom, which generally serve the purposes of food.

In support of this latter view, great importance has been placed on some recent observations of M. Lewy†, communicated to the French Academy of Sciences, in which it is stated, that when purified bees'-wax is boiled with a concentrated solution of caustic potash, or when cerine, one of the principal constituents of wax, is heated with potash and lime at the temperature of a metallic bath, it undergoes saponification, and affords a combination entirely soluble in water, and from which acids separate a fatty body having the properties and composition of stearic acid.

This statement, apparently so entirely at variance with what had hitherto been published on the nature of this substance and its behaviour towards the alkaline bases, and the ease, moreover, with which, if confirmed, pure stearic acid might in future be obtained, induced us to repeat some of the experiments of M. Lewy bearing on this point.

Before, however, detailing the results at which we arrived,

* *Annales de Chimie et de Physique*, t. iv. p. 208.

† *Comptes Rendus*, No. xiv. April 3, 1843, p. 675.

it will perhaps be well to give in brief outline the data obtained by former investigators.

According to the researches of MM. Boudet, Boissenot*, and Ettling†, wax is a mixture of cerine and myricine, which may be readily separated from each other by means of alcohol, the myricine being nearly insoluble in that medium: the cerine which is deposited on the cooling of the alcoholic solution is itself a compound body consisting of ceraine and margaric acid; these may be separated by treatment with caustic potash, which forms a soap with the margaric acid without acting at all on the ceraine. Ettling analysed ceraine and myricine, and found them to be isomeric, and composed, in 100 parts, of—

	Ceraine.	Myricine.
Carbon . . .	80·44	80·01
Hydrogen . .	13·75	13·85
Oxygen . . .	5·81	6·14

MM. Hess‡ and Van der Vleit§ regard wax as a simple substance, which in the common yellow wax is in combination with a colouring matter, and in the white wax with cerainic acid, composed of

Carbon . . .	81·52
Hydrogen . .	13·23
Oxygen . . .	5·25

Hess states that it contains no margaric acid, and does not afford either cerine or ceraine.

The experiments of Ettling, as to wax being a compound body consisting of cerine and myricine, are confirmed however by M. Lewy, who finds them to be isomeric, and composed, in 100 parts, of—

Carbon . . .	80·31
Hydrogen . .	13·38
Oxygen . . .	6·30

Berzelius, in the third German edition of his 'Manual of Chemistry,' vol. vi. p. 513, states, that wax is converted into a kind of soap by caustic alkalies, but the combination formed is of difficult solution in water, and separates in a cream-like form on the surface of the liquid; that this cream may be melted to a very hard soap, but that acids separate the *wax* with nearly unaltered properties.

On boiling wax for six hours with caustic potash we ob-

* *Journ. de Pharm.* vol. xiii. p. 43.
† *Annalen der Pharmacie*, vol. ii. p. 253.
‡ *Annal. der Pharm.* xxvii. p. 8.
§ *Bulletin de Nèerlande*, No. xvii. 1838.

served exactly the appearances described by Berzelius; it was evidently acted upon, increased in bulk, and a curdlike mass, sparingly soluble in water, separated on the top of the liquid. On melting wax and then dropping fused caustic potash into it, a small quantity of gas is given off, and the whole mass in a few seconds is converted from a liquid state into a thick, gelatinous, amber-coloured soapy substance, which was found to be almost entirely soluble in a large quantity of water. It was separated from the solution, in a curdy state, by the addition of common salt, washed, redissolved and hydrochloric acid added; this threw up a colourless oily liquid, which on cooling solidified into a waxy brittle substance. After being well washed with boiling water to remove any traces of hydrochloric acid, it was treated with alcohol, in which, with the assistance of heat, it was perfectly soluble, and on cooling separated in a crystalline state. From these appearances, we were inclined to entertain the idea that a conversion of the wax into stearic acid had taken place, but the alcoholic solution of the supposed acid did not in the least affect blue litmus paper, and when boiled with a solution of carbonate of soda not a trace of gas was evolved. Its melting point was ascertained to be 74° C., and the fused mass on cooling exhibited not the slightest trace of crystalline structure; it could not evidently therefore be stearic acid, and such was proved to be the case by the annexed analysis.

0·346 grm. of the substance, dried for six hours in the water-bath to remove all trace of alcohol, afforded on combustion with chromate of lead 0·427 grm. of water and 1·005 grm. of carbonic acid, or in 100 parts,—

Carbon . . .	80·31
Hydrogen . . .	13·70
Oxygen . . .	5·99

It is therefore as widely different from stearic acid as any body can be—the alcoholic solution of which distinctly reddens litmus paper, expels carbonic acid from carbonate of soda, solidifies into a mass, having a decided crystalline structure, and whose composition was found by Liebig, Redtenbacher and other chemists, to be carbon 76·69, hydrogen 12·70, and oxygen 20·61.

On comparing the results obtained in our analysis, it will be however immediately seen that this substance has exactly the same composition assigned by Ettling to ceraine, with which it is therefore isomeric, if not identical. The peculiar characters of ceraine are that it melts at 70° C., and on cooling forms a hard brittle mass. It is not soluble in cold alcohol,

and but very slightly in hot; on the cooling of the alcoholic solution it becomes gelatinous, but may on slow cooling be obtained in a crystalline state; it is not saponifiable. The body we have examined melts at 74° C., forms on cooling a hard brittle waxy mass, but it dissolves readily in hot alcohol, from which it crystallizes on cooling; it affords a kind of soap with potash; it does not expel carbonic acid from carbonate of soda, and has no acid properties. It will be seen that the results we have obtained agree closely with those described by Berzelius and by Ettling. On a future occasion we hope to bring before the Society an account of several curious phænomena we have observed in our experiments on this subject; for the present, we propose for the body we have examined the name of *Pseudo-ceraïne*, until by further experiments we shall have removed the discrepancies which at present appear to exist between its characters and those ascribed by Ettling to ceraine.

XLII. *On the Action of Oil of Vitriol upon Ferrocyanide of Potassium.* *By* G. Fownes, *Ph.D.*

Read March 21, 1843.

WHEN finely powdered ferrocyanide of potassium is heated in a capacious flask or retort with eight or ten times its weight of concentrated sulphuric acid, the white pasty mass first produced by the action of the acid upon the salt, gradually dissolves and disappears, its solution being accompanied by the disengagement of a prodigious quantity of permanent gas. This gas when collected over water is colourless and transparent; it has a very faint garlic odour, does not render lime-water turbid, takes fire on the approach of a taper, and burns with a bright blue flame, generating carbonic acid. When mixed with half its bulk of pure oxygen, introduced into the siphon-eudiometer and fired by the electric spark, a contraction occurs amounting to one-third part of the whole, and the residual gas becomes almost entirely absorbable by caustic potash. These characters are sufficient to prove that the gas in question is pure carbonic oxide.

When the oil of vitriol is first poured upon the ferrocyanide, a good deal of heat is produced, and the odour of hydrocyanic acid is for a moment perceptible; this disappears, however, as soon as the effervescence commences, and is replaced by a trace of formic acid vapour, which may be remarked during the whole period of the experiment. At the close of the reaction a little sulphurous acid also may be recognised; the cause of this will become immediately apparent.

If, the disengagement of carbonic acid having ceased, heat be still applied to the now fluid contents of the vessel, the escape of sulphurous acid becomes more and more marked, while at the same time a number of little white pearly crystalline plates may be observed floating about in the boiling liquid. These scales rapidly increase in number until, after the lapse of fifteen or twenty minutes from the time the first were seen, they cover the bottom of the flask to a considerable depth, glittering, when agitated, like new-formed crystals of thionurate of ammonia.

When the whole has cooled, the acid may be poured from the crystalline deposit, and the latter washed once or twice by decantation with cold water and then transferred to a paper filter. When the liquid which passes tastes no longer *strongly* acid and astringent, the filter and its contents may be spread upon a few folds of bibulous paper and placed to dry over a surface of sulphuric acid in the vacuum of the air-pump.

The acid liquid from which the crystals were deposited, is found on examination to contain in solution peroxide of iron and the sulphates of potash and ammonia.

The new substance when dry presents a very beautiful appearance, resembling, as before remarked, thionurate of ammonia; under the microscope it is seen to consist of small transparent 6-sided tables. It may be heated to above 300° F. without loss of weight or alteration of any kind; at a red heat it is slowly decomposed, leaving red oxide of iron with some sulphate of potash. It is, as the mode of preparation shows, insoluble in cold water, nevertheless a lengthened sojourn in contact with that liquid brings about slow decomposition; a little free sulphuric acid prevents this change; hence in preparing the substance, the necessity of avoiding prolonged washing, even with cold water, as the salt begins to change and grow red as soon as the free acid has been removed. With boiling water the change is immediate; the substance assumes the colour of rust, and peroxide of iron is dissolved out. Alkalies decompose it instantly, oxide of iron, retaining the crystalline appearance of the new body itself, is separated, and the solution after filtration is found to contain abundance of sulphuric acid. Carbonate of potash with the aid of heat disengages ammonia; the oxide of iron is not in this case separated, but remains in solution, communicating to the alkali a deep red colour; the addition of water, however, causes the deposition of the oxide. These characters suffice to point out the general nature of the substance under examination.

A portion carefully dried *in vacuo* was next subjected to analysis:—

20 grs. dissolved in hot hydrochloric acid and precipitated by ammonia gave 6 grs. of oxide of iron, and the filtered solution, evaporated to dryness and ignited with the usual precautions, afforded 2·9 grs. of sulphate of potash, equivalent to 1·58 grs. of potash.

20 grs. of the substance, dissolved in hydrochloric acid and precipitated by chloride of barium, gave 34·4 grs. of ignited sulphate = 11·8 grs. of sulphuric acid.

20 grs. of the substance, digested with ammonia and filtered, gave of oxide of iron 5·9 grs.; the solution by precipitation with baryta afforded 34·2 grs. of sulphate = 11·74 grs. of sulphuric acid.

100 parts will therefore contain, if the ammonia be taken by difference,—

Sulphuric acid . . .	59·0	58·7
Peroxide of iron . . .	30·0	29·5
Potash	7·9	
Oxide of ammonium .	3·1	
	100·0	

A separate specimen, the result of another operation, gave numbers closely coinciding with the above.

It will be seen that the relation of the sulphuric acid to the oxide of iron is almost exactly that which exists in common iron-alum; the formula

$$2\,(Fe_2O_3, 3SO_3) + \begin{matrix} KO, SO_3 \\ NH_4O, SO_3 \end{matrix}$$

gives, reckoned to 100 parts,—

Sulphuric acid	58·0
Peroxide of iron . . .	28·8
Potash	8·5
Oxide of ammonium . .	4·7
	100·0

Taking into account the impossibility of completely washing the crystals without causing decomposition, a comparison of the calculated and found results will perhaps be deemed satisfactory.

This anhydrous iron-alum is apparently the type of a number of crystalline anhydrous sulphates which may be formed under similar circumstances. For example, when green vitriol in powder is boiled with strong sulphuric acid it is dissolved, sulphurous acid is disengaged, the protoxide of iron passing to peroxide, which, as fast as it is formed, falls down in combination with the acid as a crystalline pinkish-white powder.

Anhydrous sulphates of copper and nickel may be obtained by a similar process; also the double sulphate of nickel and potash. The copper salt has a beautiful lilac colour; that of nickel is bright yellow. All these compounds are, however, changed by contact with water; the persulphate of iron is the most stable, but even that ends by dissolving in great part.

There is no difficulty in explaining the decomposition undergone by the ferrocyanide of potassium under the influence of the acid, and its conversion into the products observed.

1 equivalent of ferrocyanide of potassium and 9 equivalents of water contain the elements of 6 equivalents of carbonic oxide, 3 equivalents of ammonia, 2 equivalents of potash, and 1 equivalent of protoxide of iron.

1 eq. ferrocyanide potassium =	6 eq. carbon.	6 eq. carbonic oxide.
	3 „ nitrogen.	
	2 „ potassium.	2 eq. potash.
	1 „ iron.	1 eq. protox. iron.
9* eq. water. . . . . =	6 „ oxygen.	
	2 „ oxygen.	
	1 „ oxygen.	
	9 „ hydrogen.	3 eq. ammonia.

At a subsequent period, when the evolution of carbonic oxide ceases and the temperature rises very high, the iron becomes peroxidized at the expense of a portion of the acid, sulphurous acid is emitted, and the iron-alum gradually formed, the excess of alkaline sulphates remaining in solution.

In conclusion, it may be worth while calling the attention of those whom it may concern to the foregoing experiments, as furnishing an extremely easy and œconomical method of preparing carbonic oxide for purposes of research or demonstration. A single half-ounce of the yellow salt treated with some oil of vitriol in a common Florence flask fitted with a perforated cork and conducting tube, gives more than 300 cubic inches of gas, which has all the marks of the most perfect purity: it does not in the least affect lime-water, and becomes entirely converted into carbonic acid by explosion with half its volume of oxygen. The gas given off during the whole of the reaction is equally pure, except quite at the end of the operation, when, as before noticed, a little sulphurous acid appears.

* Probably 6 eq. from the oil of vitriol, the acid of which has combined with the ammonia, potash and oxide of iron, and 3 eq. being the water of crystallization of the salt.

INDEX TO THE MEMOIRS.

VOL. I.

ACIDS:—products of the action of, on castor oil, 1; œnanthylic, 2; malic, 28; employment of chromic, as an agent in voltaic arrangements, 61; conversion of benzoic, into hippuric, in the animal œconomy, 79; preparation of hydrocyanic, 96; pyrogallic, 127, 132; garden rhubarb as a source of malic, 193; action of nitric, upon theine, 219; ferric, 240.

Acetate of silver, 24.

Æther, œnanthylic, formation of, 2; analysis of, 3.

Æthogen, preparation of, 149; properties of, 150.

Æthonides, 149.

Æthyl, fumarate of oxide of, analysis of, 34.

Alkalies, action of, on wax, 248.

Ammonia, supposed part which the nitrogen of the atmosphere plays in the formation of, 197.

Ammonium, cadmio-chloride of, 105.

Analyses:—œnanthylic acid, 2; æther, 3; œnanthylate of silver, 4; of baryta, 4; acetate of silver, 24; tartrate of, 24; racemate of, 24; malate of, 24, 33; tartrate of lead, 25; racemate of, 25; tartrate of, and racemate of, 25; malate of lime, 30; magnesia, 31; zinc, 32; copper, 33; barytes, 34; strontian, 34; fumarate of oxide of æthyl, 34; fumaramide, 35; cetine, 43; ethal, 44; laurel turpentine, 45; oil of hyssop, 46; of assafœtida, 48; chloride of cacoplatyl, 65; bromide of, 66; iodide of, 67; sulphate of the oxide of, 69; of a new oxalate of chromium and potash, 89; of theine, 220; of fat from various mines, 231; of theine prepared by sublimation, 237; of theine from Paraguay tea, 238; of ceraine and myricine, 249; of pseudoceraine, 251.

Archil, on substances contained in the lichens used for preparations of, 71.

Arrott (Alexander R.) on some new cases of voltaic action, and on the construction of a battery without the use of oxidizable metals, 142.

Assafœtida, oil of, analyses of, 48.

Balmain (W. H.) on æthogen and æthonides, 149.

Baryta, formation of, œnanthylate of, 4; analysis of, 4.

Barytes, analysis of, malate of, 34.

Beetz (W.) on the spontaneous change of fats, 230.

Benzoic acid, conversion of, into hippuric acid, in the animal œconomy, 79.

Biniodide of mercury, change of colour in the, 85.

Bistort, examination of, 212.

Bunsen (Prof.) on the radical of the cacodyl series of compounds, 49; on a new class of cacodyl compounds containing platinum, 63.

Cacodyl series of compounds, radical of the, 49; isolation of, 49; formation of the compounds of, from their radical, 54; decomposition of the radical, 55; compounds, new class of, containing platinum, 63.

Cacoplatyl, chloride of, 64; analysis of, 65; bromide of, 66; analysis of, 67; iodide of, 67; analysis of, 68; sulphate of the oxide of, 68; analysis of, 69.

Cadmium, salts of, 104.

Campbell (R. Corbett) on the ferrocyanides, 38.

Carbon, atomic weight of, 9.

Cashew nut, examination of the, 212.

Castor oil, products of the action of nitric acid on, 1.

Catechu, examination of, 141.

Cetine, analyses of, 43.

Ceraine, analysis of, 249; pseudo, examination and analysis of, 251.

Chamellia Japonica, examination of, 219.
Chatterly (W. M. F.) on saline manures containing nitrogen, 152.
Chloride of cacoplatyl, 64; analyses of, 65.
Chromates and sulphates of the potash family, 116.
Chromic acid, employment of, as an agent in voltaic arrangements, 61.
Chromium and potash, new oxalate of, 89; analysis of, 90; red oxalate of, 93.
Cock (W. J.) on palladium, its extraction, alloys, &c., 161.
Combinations, heat disengaged in, 106.
Cooper (J. T.) on certain improvements in the instrument invented by the late Dr. Wollaston for ascertaining the refracting indices of bodies, 234.
Copper salt, crystallization of, 5.
Copper, acid malate of, and analyses of, 33; constitution of the subsalts of, 221; trisulphate of, 222; tetrasulphate of, 223; pentasulphate of, 225; subsulphates, tabular arrangement of, 230.
Cow, changes in the composition of the milk of the, 174.
Croft (Henry) on a new oxalate of chromium and potash, 89; on some salts of cadmium, 104.
Cudbear, on substances contained in the lichens used for the preparation of, 71.
Cyanate of potash, preparation of, 97.
Cyanide of potassium, preparation of, and its applications, 94; as a reducing agent, 97; as an agent of separation in quantitative analysis, 98.
Cyanurate of potash, on the acid, 42.
Detmer (M.) on bleaching salt, 6.
Divi-divi, examination of, 140.
Ethal, analyses of, 44.
Eucalyptus, sugar of the, 159.
Everitt (Thomas) on the leaf-stalks of garden rhubarb as a source of malic acid, 193.
Fat, formation of, in the animal body, 164; spontaneous change of, 230; analysis of, from various mines, 231.
Ferrocyanides, on the, 38; of potassium, action of oil of vitriol upon, 251.
Fownes (George) on the preparation of artificial yeast, 100; on the action of oil of vitriol upon the ferrocyanide of potassium, 267.
Francis (W.) on the action of alkalies on wax, 248.
Fumaramide, analysis of, 35.
Garrod (Alfred Baring) on the conversion of benzoic acid into hippuric in the animal œconomy, 79.
Graham (Thomas) on the constitution of the sulphates as illustrated by late thermometrical researches, 82; on the heat disengaged in combinations, 106.
Gregory (Dr. W.) on a new method of obtaining pure silver, either in the metallic state or in the form of oxide, 190.
Gum kino, examination of, 141.
Hagen (Robert) on malic acid, and the changes undergone by its salts at high temperatures, 28.
Heat, as disengaged in combinations, 106.
Hippuric acid, conversion of benzoic acid into, in the animal œconomy, 79.
Hydrocyanic acid, preparation of, 96.
Hyssop, oil of, analyses of, 46.
Iron, composition of an acid oxide of, 240.
Johnston (J. F. W.) on the sugar of the Eucalyptus, 159.
Larch bark, examination of, 213.
Lead, and its oxides, atomic weight of, 14; tartrate of, and racemate of, 25; pyrogallate of, 130; æthonide of, 151.
Lecanorin, 73; decomposition of, 75.
Lichens, on substances contained in the, employed for preparations for archil and cudbear, 71.
Liebig (Prof.) on the atomic weight of carbon, 9; on the preparation of cyanide of potassium, and on its applications, 94; on the formation of fat in the animal body, 164.
Lime, malates of, analyses of, 29; acid malate of, 30.
Magnesia, malates of, analyses of, 31.
Magnesian sulphates, hydration of, 111.
Malates, of silver, 24, 33; of lime, 29; magnesia, 31; zinc, 32; copper, 33; barytes, 34; strontian, 34; at high temperatures, 35.
Malic acid, 28.

Manures, saline, containing nitrogen, 152.
Mercury, biniodide of, change of colour in the, 85.
Metals, oxidizable, on the construction of a battery without the use of, 142.
Milk of the cow, changes in the composition of the, 174.
Molecules of a body, re-arrangement of the, after solidification, 77.
Muriatic acid, action of, upon tannin, 137.
Myricine, analyses of, 249.
Myrobalans, examination of, 210.
Nitric acid, products of the action of, on castor oil, 1; on theine, 219.
Nitrogen, saline manures containing, 152; estimation of, in organic compounds, and on the part which that of the atmosphere plays in the formation of ammonia, 197.
Nitro-theine, 239.
Oak bark, examination of, 139.
Œnanthylate of silver, preparation of, 3; analysis of, 4; of baryta, formation and analysis of, 4; of potash, 5; of strontian, appearance of, 5.
Œnanthylic acid, formation and analysis of, 2; æther, formation of, 2; analysis of, 3.
Oxalate of chromium and potash, new, 89; analysis of, 90; red oxalate of, 93.
Oxide, new method of obtaining pure silver in the form of, 190.
Palladium, its extraction, alloys, &c., 161.
Pentasulphate of copper, 225.
Paraguay tea, theine found in, 217, 238.
Playfair (Dr. Lyon) on the changes in composition of the milk of a cow, according to its exercise and food, 174.
Platinum, on a new class of cacodyl compounds containing, 63.
Polygonum bistortus, examination of, 212.
Pomegranate rind, examination of, 213.
Potash, formation of œnanthylate of, 5; acid cyanurate of, 42; and chromium, new oxalate of, 89; analysis of, 90; red oxalate of, 93; preparation of cyanate of, 97.
Potassium, cyanide of, preparation of and its applications, 94; as a reducing agent, 97; as an agent of separation in quantitative analysis, 98; cadmio-chloride of, cadmio-bromide of, cadmio-iodide of, 105; æthonide of, 150; action of oil of vitriol on ferrocyanide of, 251.
Pseuderythrin, 76.
Pseudoceraine, examination and analysis of, 251.
Pyrogallate of lead, 130.
Pyrogallic acid, 127; astringent substances as sources of, 132.
Pyroxylic spirit, on, 36; table of specific gravities of, 37.
Racemate of silver, 24; of lead, 25.
Redtenbacher (Prof.) on the atomic weight of carbon, 9.
Reiset (M.) observations on his remarks on the new method for the estimation of nitrogen in organic compounds, 197.
Rhubarb, leaf-stalks of garden, as a source of malic acid, 193.
Ricinus communis, examination of the products of the oxidation of the oil of, 1.
Salts, bleaching, 6.
Schunck (Edward) on some of the substances contained in the lichens employed for the preparation of archil and cudbear, 71.
Silver, œnanthylate of, 3; table of experiments with acetate, tartrate, racemate, and malate of, 24; æthonide of, 152; new method of obtaining pure, 190.
Smith (J. D.) on the constitution of the subsalts of copper, 221; on the composition of an acid oxide of iron, 240.
Soda, sulphate of, 118; bisulphate of, 121.
Sodium, cadmio-chloride of, 105.
Stearine, analysis of, by Liebig and Pelouse, 231.
Stenhouse (Dr. John), examination of cetine, ethal, oils of laurel turpentine, hyssop, and assafœtida, 43; on pyrogallic acid, and some astringent substances which yield it, 127; on some astringent substances as sources of pyrogallic acid, 132; examination of astringent substances, 208; on theine and its preparation, 215; on theine, 237.
Strontian, appearance of œnanthylate of, 5; malate of, analysis of, 34.
Subsalts of copper, constitution of the subsulphates, 221.

Sugar of the Eucalyptus, on the, 159.
Sulphates, constitution of, 82; magnesian, hydration of, 111; and chromates of the potash family, 116; double, 120.
Tannin, action of muriatic acid upon, 137.
Tartrate of silver, 24; of lead, 26.
Tea, black and green, examination of, 208; tannin of, 209; Paraguay, 217, 238.
Temperatures, malates at high, 35.
Tetrasulphate of copper, 223.
Theine, and its preparation, 215; found in Paraguay tea, 217, 238; analysis of, 220; action of nitric acid upon, 219; analysis of, prepared by sublimation, 237; formula for, 238.
Tilley (T. G.) on some of the products of the action of nitric acid on castor oil, 1.
Trisulphate of copper, 222.
Turpentine, laurel, analysis of, 45.
Ure (Dr.) on the successive strengths of pyroxylic spirit, corresponding to its successive specific gravities, with some introductory observations, 36.
Valonia, examination of, 139.
Vitriol, hydration of, oil of, 107; action of oil of on ferrocyanide of potassium, 251.
Voltaic arrangements, employment of chromic acid as an agent in, 61.
Voltaic action, on some new cases of, 142.
Warington (R.) on the employment of chromic acid as an agent in voltaic arrangements, 61; on a re-arrangement of the molecules of a body after solidification, 77; on the change of colour in the biniodide of mercury, 85; on the red oxalate of chromium and potash, 93; on the action of alkalies on wax, 248.
Wax, action of alkalies on, 248.
Will (Dr.) on M. Reiset's remarks on the estimation of nitrogen in organic compounds, 197.
Wollaston (Dr.), improvements in the instrument invented by the late, for ascertaining the refractive indices of bodies, 234.
Yeast, preparation of artificial, 100.
Zinc, malates of, analyses of, 32; acid, 32; basic malate of, 33; æthonide of, 151.

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